**VTT Technical Research Centre of Finland**

# Spinning of cellulose fibres from ionic liquid solution

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TEKNILLINEN TIEDEKUNTA

# Spinning of cellulose fibres from ionic liquid solution

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Ympäristötekniikka

Diplomityö

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# TIIVISTELMÄ

Selluloosakuitujen kehräys ionisesta liuottimesta

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Oulun yliopisto, Ympäristötekniikka

Diplomityö + 2021, 79 s.

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Tämän diplomityön tavoitteena oli tutkia yhdeksän eri tavoin esikäsitellyn kraftsellunäytteen liuotusta uudentyyppiseen ioniseen liuottimeen ([mTBNH][OAc]) sekä selvittää, miten esikäsittelyt vaikuttavat kuidun kehräykseen ja valmiin kuidun mekaanisiin ominaisuuksiin.

Näytteet saapuivat kuivattuina, josta johtuen näytteisiin oli aiheutunut hornifikoitumista. Hornifikaation peruuttamiseksi vesiaktivointia kokeiltiin kolmella eri menetelmällä, joista parhaaksi valikoitui menetelmä, jossa massan mekaaninen vaivaus yhdistettiin turvotukseen suuressa määrässä vettä, ja kuivaukseen vetokaapissa.

Sellunäytteet sekoitettiin ioniseen liuottimeen huoneenlämmössä, jonka jälkeen näytteiden liuotus tapahtui noin 85 °C lämpötilassa. Näytteiden liukoisuudella ei ollut selkeää korrelaatiota esikäsittelyn laadun kanssa: Kaikki näytteet liukenivat yhtä huonosti ennen vesiaktivointia, mutta yhtäläisen hyvin vesiaktivoinnin jälkeen.

Näytteiden kehräys toteutettiin ilmarakoa hyödyntävällä märkäkehruutekniikalla, erikoisvalmisteisella kehruulaitteistolla. Näytteet pumpattiin 8-reikäisen 50 µm suulakkeen läpi kehruuhauteen kautta galetille, näytteiden kehrättävyydestä riippuvalla nopeudella. Kehrättävyyttä pyrittiin parantamaan liuoksen esilämmityksellä, pumppauksen aikaisella lämmityksellä, ja selluloosakonsentraatiota laskemalla. Lopulta kehrättävyyden kannalta optimaaliseksi konsentraatioksi paljastui 5 m% sellunäytettä liuoksen kokonaismassasta.

Yhdeksästä näytteestä kuudella oli tarpeeksi hyvä kehrättävyys, jotta saatiin kuituja mekaaniseen testaukseen asti. Näytteistä kolmella oli selkeästi muita paremmat mekaaniset ominaisuudet: Havusellunäyte SW5 ja Eukasellunäyte HW3 olivat molemmat esikäsitelty endoglukanaasilla ja kylmäalkaliuutolla, josta johtuen näillä näytteillä oli pienin kokonaismäärä hemiselluloosaa koko tutkimuksessa, varsinkin ksylaanin osalta. Happokäsitellyllä havusellunäytteellä SW3 oli hieman keskimääräistä korkeampi hemiselluloosapitoisuus, mutta happokäsittelyn luonteesta johtuen kaikista matalin intrinsinen viskositeetti tämän tutkimuksen näytteistä. Loppupäätelmänä sellunäytteen kehrättävyydessä yksi tärkeimmistä prosessiparametreistä on kehruuliuoksen viskositeetti, johon hemiselluloosalla ja varsinkin ksylaanilla on kasvattava vaikutus. Näytteen SW3 kohdalla hemiselluloosan aiheuttamaa viskositeetin nousua kompensoi selluloosan polymerisaation asteen laskeminen happokäsittelyn myötä, joka osaltaan selittää tutkimustuloksia.

Lopulta näytteet tutkittiin mekaanisen testauksen lisäksi myös optisella mikroskoopilla. Kuitujen pintarakenteella ja paksuudella oli selvää korrelaatiota kehrättävyyden kanssa: Hyvä kehrättävyys johti selkeästi tasaisempaan rakenteeseen niin paksuuden kuin pintarakenteenkin suhteen. Suurehkon hemiselluloosapitoisuuden todettiin mahdollisesti vaikuttavan pintarakenteeltaan epätasaisempien kuitujen morfologiaan, mikä samalla selittäisi paremmin kehräytyneiden kuitujen selkeästi tasaisempaa pintarakennetta.

*Asiasanat: Kraft-sellu, Ioninen liuotin, Märkäkehruu, Keinokuitu*

# ABSTRACT

Spinning of cellulose fibres from ionic liquid solution

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University of Oulu, Degree Programme of Environmental Engineering

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Supervisor at VTT: Taina Kamppuri

The goal of this master's thesis was to study the solubility of nine different kraft pulp samples with different pre-treatments into a novel ionic liquid ([mTBNH][OAc]), and to find out how these pre-treatments affect the spinnability of dopes and mechanical properties of produced fibres.

Samples were delivered in dried form, resulting in hornification of samples. Effect of hornification was reversed by kneading the pulp sample, combined with swelling in large amount of water and drying in draft cabinet was deemed the best method.

Pulp samples were mixed into ionic liquid in room temperature, after which they were dissolved in temperature of approximately 85 °C. It was concluded that there was no correlation between solubility and pre-treatments pulp samples had undergone: Every sample had equally poor solubility before water activation, but solubilities were fully restored after treatment.

Spinning of samples was conducted by dry-jet wet spinning process, utilizing custom-made spinning equipment. Samples were extruded through spinneret with eight 50 µm holes and drawn to godet through coagulating bath consisting of water. Efforts were made to improve the spinnability of dopes either by pre-heating of samples, heating samples during spinning, or lowering the cellulose concentration of dopes. Optimal concentration for spinnability was found to be 5 wt% of cellulose from total mass of dope.

From nine samples, six had sufficient spinnability to produce fibres for mechanical testing. From these samples, SW3, SW5, and HW3 had clearly superior mechanical properties compared to others. It was found that viscosity of dope was one of the most important process parameters regarding spinnability of dopes, which was most effectively decreased by treatment with endoglucanase and could caustic extraction in case of samples SW5 and HW3, or with acid hydrolysis in case of sample SW3. Viscosity of dope is increased by amounts of hemicelluloses and especially xylan, which makes their removal beneficial for reduction of dope viscosity. With sample SW3, viscosity was lowered by depolymerization of cellulose.

Samples were also studied with optical microscope. Surface structure and thickness had clear correlation with spinnability: Good spinnability of dope caused produced fibre to have clearly smoother surface structure compared to samples with inferior spinnability. It was noted that high amounts of hemicelluloses might cause uneven surface morphology, which also explains the smooth structure of samples with better spinnabilities.

*Keywords: Kraft pulp, Ionic liquid, Dry-jet wet spinning, Man-made fibre*

# PREFACE

The Master's thesis was performed at VTT Technical Research Center of Finland as a part of GRETE project in Tampere. This thesis is a part of a project that has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 837527.

The subject for this master's thesis was chosen as meaningful continuation for my studies of bioproduct engineering, and my previous employment in paper industry. These past events caused my interests to grow towards pulp industry and research for new and interesting uses for wooden biomass. I am thankful for VTT for this opportunity to study this interesting process and continue working in future projects after this master's thesis.

When I started this project, I though this would test everything I learned in my university studies thus far. I was wrong, as this project taught more than I could have ever imagined.

As supervisor for this thesis, Taina Kamppuri at VTT gave her full support for this thesis work, both in laboratory work and in literature part. If there were problems with process, it was fixed right away. I also thank my supervisors Elisa Koivuranta and Henrikki Liimatainen at university of Oulu. You gave lots of valuable insight into writing process, which I really appreciate.

I also thank my partner Heini Mäkelä and my dog Minni for their continuing support through this process.

This master's thesis was performed between 23.10.2020 and 03.09.2021 at Tampere.

Tampere, 04.09.2021

Simo Hannula

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| CCE | Cold caustic extraction |
| DMC | Dry matter content |
| DP | Degree of polymerization |
| DR | Draw ratio |
| DWM | Dry wood mass |
| MW | Average molecular weight |
| MWD | Molecular weight distribution |

# 1 INTRODUCTION

Cellulose is the most abundant biopolymer on earth (Isogai et al., 2011; Li et al., 2018), which humankind have utilized from the moment tools and fire were discovered. Even though most of human history wood has been used for warmth and as building material, more sophisticated methods for utilizing cellulose started to emerge in China almost 2000 years ago, when paper was first produced by cooking inner bark of mulberry tree in a solution of wood ash (Gustafsson et al., 2011).

Until the second half of the 19$^{th}$ century, paper was mainly produced manually from annual plants and rags. Due to increasing demand for paper, wood was considered as raw material, and first patent for pulping wood with sulfuric acid was given in 1866 for American chemist B.C. Tilghman (Gustafsson et al., 2011). This method utilized sulfuric acid with calsium bisulphite, thus the name “sulphite pulping”. First real mill producing sulphite pulp was established in Sweden in 1871 (Gustafsson et al., 2011).

At roughly the same time, people were conducting research of pulping with sodium hydroxide, and the first mill utilizing soda process was built in the USA in 1860 (Gustafsson et al., 2011). Pulping process was improved in 1871 by adding sulphides in cooking liquor, and again in 1879, when it was discovered that sodium carbonate could be replaced with crystalline decahydrate sodium sulphate, which is why this alkaline pulping process is sometimes called “sulphate pulping”(Gustafsson et al., 2011). Sulphite of the cooking liquor made the cooking process faster and resulting pulp stronger. Therefore this process became known as ”kraft” pulping, which means strength in German and Swedish (Gustafsson et al., 2011). Kraft pulping had some drawbacks though: The pulp was darker than pulp produced with sulphite process, was more difficult to bleach and refine, and the process produced malodorous gases. During the years process got many improvements, and by the year 1937, it finally surpassed sulphite process as the most widely used pulping method (Gustafsson et al., 2011). Nowadays, about 80% of chemical pulp is produced with kraft process (Fernández-Rodríguez et al., 2019).

There are many reasons why kraft method gained more popularity, compared to sulphite method. Sulphide in kraft liquor causes fast delignification, which decreases cooking times and produces stronger pulp. Chemicals and energy are easily recoverable, and

process can be utilized with wide variety of wood species (Gustafsson et al., 2011). In addition, kraft process produces valuable byproducts like tall-oil and turpentine, which improves economic aspect of pulping process (Gustafsson et al., 2011). Even though initial brightness of kraft pulp is still lower than with sulphite pulp and process still produces malodorous organic sulfides, modern bleaching and gas scrubbing technology have resolved those problems (Gustafsson et al., 2011).

Sulphite process can be utilized in wide range of pH, which is useful when manufacturing specialty pulps with optimized process conditions (Gustafsson et al., 2011). Sulphite process has also better carbohydrate yield at given brightness, less odor problems than kraft process, and smaller investment costs (Gustafsson et al., 2011). Drawbacks of sulphite pulping include high biological oxygen demand of process effluents, and high amounts of sulfur dioxide emissions (Gustafsson et al., 2011). Process is also incompatible with several species of wood, because of the inability of process to dissolve some extractives (Gustafsson et al., 2011).

Public interest to produce textile fibres from wood has been steadily increasing, because production of cotton can't keep up with increased need for textile which comes with fast population growth of the world (Björquist et al., 2018). So far, the need for textiles have been addressed with production of synthetic fibres like polyester, which cannot compete with cotton in comfortability like cellulose-based fibres (Björquist et al., 2018).

Man-made cellulose fibres have been around for over a hundred years, viscose-rayon, for example (Rana et al., 2014). Because drawbacks like poor resiliency, tendency to form wrinkles, poor wet tenacity, high energy consumption of production, and use of many harmful chemicals, alternatives for viscose have been subject of many researches (Rana et al., 2014). To this date, one of the most wide-spread alternatives for viscose-rayon is Lyocell, which is also produced from dissolving pulp like viscose-rayon, but manufacturing process is vastly improved. Production of Lyocell doesn't have as harsh environmental effects than viscose-rayon, has better physical properties, and used solvent can be almost completely recycled (Rana et al., 2014). Lyocell has its own drawbacks though: Degradation of used solvent produces toxic compounds, formaldehyde for example (S. Zhang et al., 2018a). In addition, negative aspects relating to use of dissolving pulp still exist, which means rather high production costs (S. Zhang et al., 2018a). Kraft pulp would be economically better choice for production of regenerated fibres, which has

raised interest to study if it could be used to produce fibres. One big difference between kraft pulp and dissolving pulp is their hemicellulose composition: Whereas dissolving pulp has very high purity and thus low hemicellulose content (Sixta, 2006 as cited in Chen et al., 2020), kraft pulp has generally quite high amounts of hemicellulose (Shackford, 2003), which might cause problems in quality of regenerated cellulose fibres (X. Jiang et al., 2020), or in runnability of process itself (Gehmayr et al., 2011). Because this study contains several pulp samples with different hemicellulose compositions, this research question will be examined further.

Because of the increasing need for cellulose-based textiles, widespread production of kraft pulp, and environmental problems in production of dissolving pulp, kraft pulp - based alternatives for dissolving pulp are being studied. The main goal of this master's thesis is to study the effects of different pre-treatments to solubilities and spinnabilities of both softwood and hardwood kraft pulp samples. In addition, both mechanical and physical properties of said fibres will be studied for the best possible development of this novel spinning process.

# 2 LITERARY REVIEW

## 2.1 Lignocellulose

### **2.1.1** Cellulose

Cellulose is a linear, homopolysaccharide molecule forming from β-D-glucopyranose -units by 1-4 glycosidic bonds (Figure 1). Because all the substituents of individual units are equatorially aligned, they have minimal change of reacting with each other, which results in very stable molecular structure (Alén et al., 2000). This molecule can have even 15000 repeating units in case of cotton, or "only" 10000 units in case of natural wood material (Alén et al., 2000). Even chemically treated pulps can contain degree of polymerization (DP) of 500-2000 units, which is quite a lot for naturally occurring polymer (Alén et al., 2000).

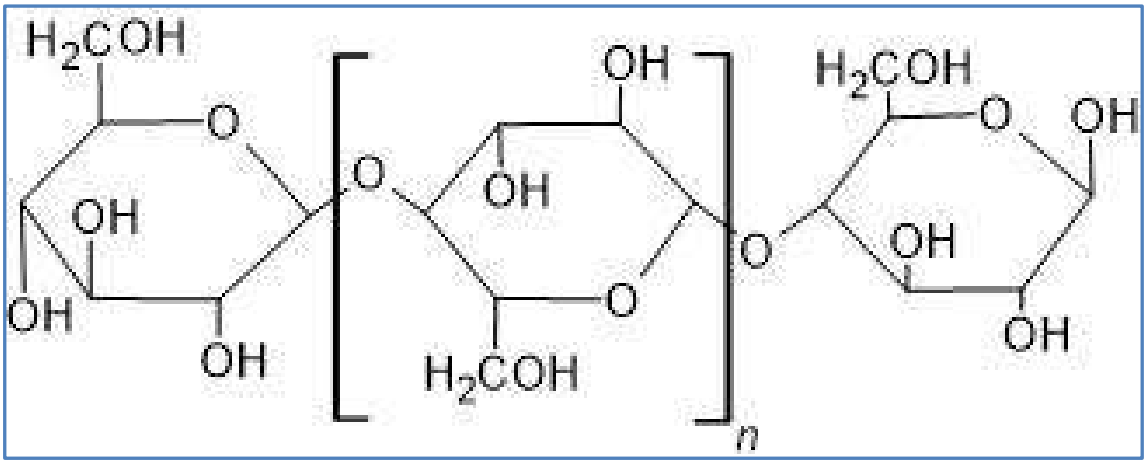


Figure 1: Structure of cellulose

In addition to stable nature of individual cellulose molecules, fibrils forming from these molecules have some exceptional properties: Cellulose molecules have three reactive hydroxyl groups in each repeating unit, which causes formation of dense network of hydrogen bonds between cellulose molecules (Figure 2), giving cellulose fibrils their high crystallinity (Alén et al., 2000), and mechanical strength properties (Isogai et al., 2011). In addition to high mechanical strength, these hydroxyl groups can be chemically

modified, which gives cellulose lots of possible applications as strong and versatile biomaterial (Isogai et al., 2011). These hydroxyl groups are also responsible of hydrophilic nature of cellulose, which gives cellulosic materials usually high water absorbency (Chami Khazraji & Robert, 2013).

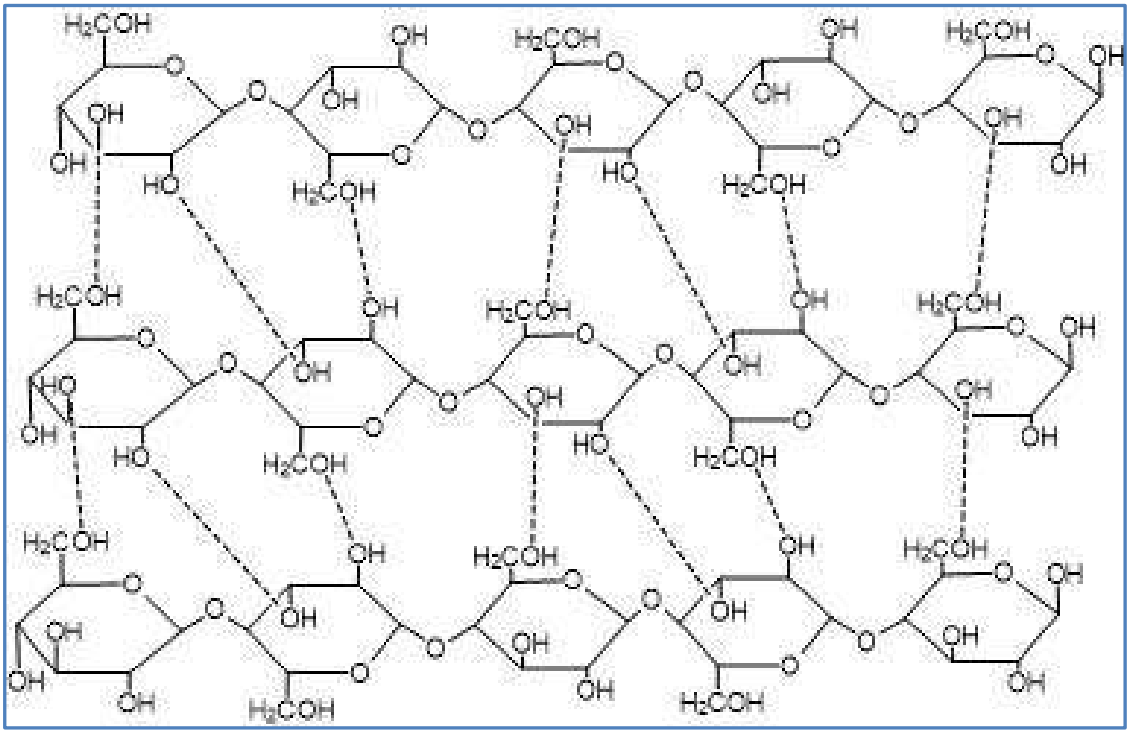

Figure 2: Hydrogen bonds between molecules

Cellulose fibrils further aggregate into microfibrils with both amorphous and crystalline regions, and finally into highly crystalline fibre wall cellulose (Alén et al., 2000). This highly crystalline structure gives cellulose fibres their high mechanical strength, but it also makes them highly resistant against chemical treatments and different solvents (Alén et al., 2000).

### **2.1.2** Hemicellulose

Whereas composition of cellulose is quite simple, hemicelluloses are a little more complex group of molecules. Like cellulose, hemicelluloses are important group of carbohydrates, from which wooden biomass is composed. Differing from homopolysaccharidic (Same repeating units) nature of cellulose, hemicelluloses are heteropolysaccharides, consisting of many different moieties, which can be divided into hexoses, pentoses, hexuronic acids, and deoxyhexoses (Alén et al., 2000). Another

important difference between hemicellulose and cellulose is their degree of polymerization and crystallinity: Whereas natural cellulose might have degree of polymerization of 15000, hemicelluloses usually have DP of only 100-200 repeating units (Alén et al., 2000). Hemicellulose doesn't have the same kind of crystalline structure as cellulose has, which makes hemicellulose more susceptible to chemical and thermal degradation (Alén et al., 2000). Some parts of hemicellulose are even soluble in water, which makes fractionation of wood constituents easier (Alén et al., 2000). Hemicelluloses are generally soluble in alkali, which can be seen with alkali-based kraft pulping (Gustafsson et al., 2011). Different hemicelluloses might react differently during pulping though, and retention of xylan might happen, especially with xylan-rich hardwood species (Carrillo et al., 2018).

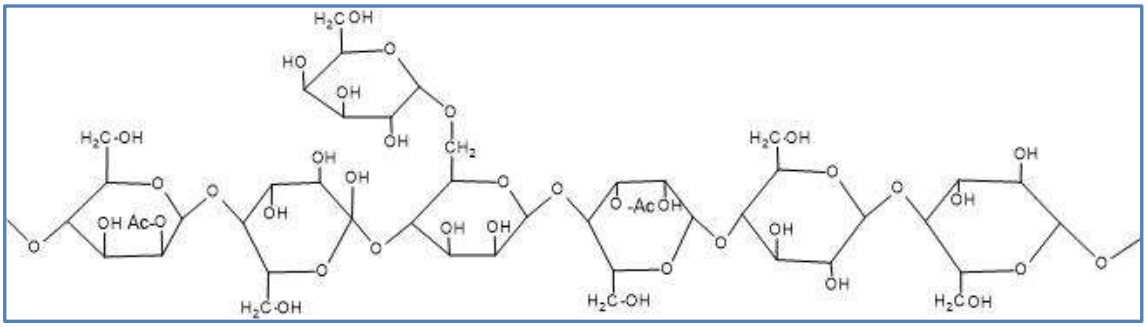


Figure 3: Partial structure of galactoglucomannan

Softwoods and hardwoods differ in their hemicellulose composition, both in quality, and quantity of different hemicelluloses. Generally speaking, softwood hemicelluloses contain more mannose and galactose units, while hardwood hemicellulose contains more xylose and acetylated hydroxyl groups (Alén et al., 2000). Softwood hemicelluloses are mainly galactoglucomannan (Figure 3) (15-20% of Dry wood mass (DWM)), and arabinoglucuronoxylan (5-10% of DWM), whereas hardwood hemicelluloses consist of glucomannan (<5% of DWM) and glucuronoxylan (20-30% of DWM) (Alén et al., 2000). Differing from hardwood xylan, softwood xylan has no acectyl groups. On the other hand, softwood xylan has more uronic acid substituents (Alén et al., 2000). With glucomannan, hardwood version has higher glucose/mannose -ratio, is not acetylated, and is unsubstituted (Alén et al., 2000). In addition to glucomannans and xylans, softwoods contain very small amounts of arabinogalactan, excluding larches which might have 20% of arabinogalactan in their heartwood (Alén et al., 2000). There are differences in hemicellulose composition of different softwood and hardwood species, and even within

specimens from same species (Miranda & Pereira, 2002). Different wood species might also exhibit different forms of seemingly same hemicelluloses (Alén et al., 2000).

### **2.1.3** Lignin

With cellulose and hemicelluloses, lignin is the third main component in lignocellulosic material. Knowledge about lignin is of great technical importance, because removal of lignin is the most important step in chemical pulping for liberation of cellulose fibres (Gustafsson et al., 2011). In addition, lignin causes discoloration of pulp stock, which is not desired when brightness of product is of great importance (Gustafsson et al., 2011). The purpose of lignin is to "glue" different wood constituents together, while supporting cell walls of plants with its rigid matrix (Gustafsson et al., 2011). Unlike cellulose and hemicellulose, structure of lignin is not regular. In addition to this irregularity, lignin can be further divided into softwood-, hardwood-, and grass lignins (Gustafsson et al., 2011). Different lignin byproducts are also produced with different pulping methods, including organosolv lignin, kraft lignin, and alkali lignin (Gustafsson et al., 2011).

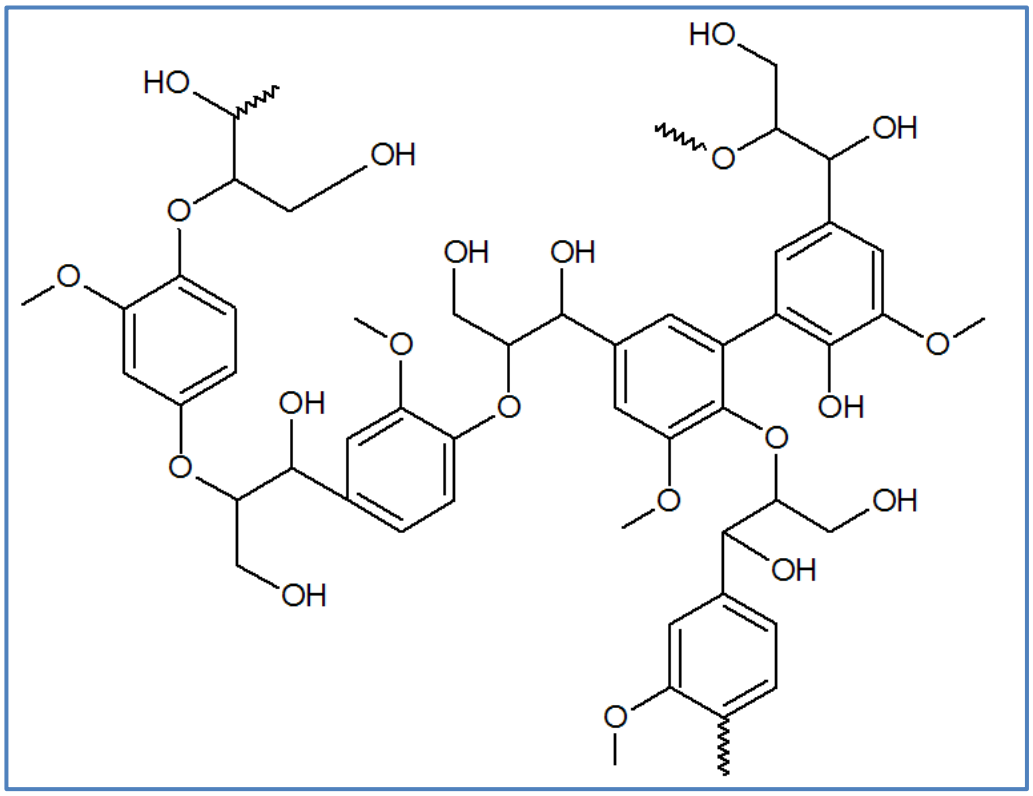


Figure 4: One possible structure for lignin (Modified from polymer properties database)

Lignin can be described as thermoplastic material with high molecular mass, consisting mainly of aliphatic hydroxyl, methoxyl, phenolic hydroxyl, and carbonyl groups, with different ratios depending on source of lignin: For example, hardwood lignin contains more methoxyl groups, in difference with more phenolic hydroxyl groups containing softwood lignin (Gustafsson et al., 2011). Lignin is composed of these units, which are connected with either ether linkages or carbon-carbon bonds, from which the former are more common with 2/3 of total linkages between units (Gustafsson et al., 2011). One possible structure for lignin can be observed above in Figure 4. Native lignins are insoluble, but once isolated, can be dissolved in solvents like acetone, or dimethyl sulfoxide, for example (Gustafsson et al., 2011). In kraft delignification, the main goal is the breakage of aryl ether bonds of lignin with strongly alkaline cooking liquor containing compounds such as NaOH and $Na_2S$ (Gustafsson et al., 2011). Because lignin cannot be liberated from wood intact, the absolute structure of lignin is not known very well (Gustafsson et al., 2011).

In addition to being matrix between other pulp constituents, lignin has also been reported to form chemical bonds with carbohydrates. These lignin carbohydrate complexes (LCC) have been found between lignin and hemicelluloses, such as xylan and glucomannan, but bonds between lignin and cellulose have also been implied (Gustafsson et al., 2011). Chemical bonds between these wood constituents have been speculated to contain at least hydrogen- and Van der Waals forces, but knowledge about these complexes is still quite limited for reasons explained before (Gustafsson et al., 2011). It is still evident, that knowledge about the nature of these bonds is important for efficient separation of cellulose in pulp industry.

### **2.1.4** Structure of wood

In addition to knowledge about chemical composition of wooden biomass, it's also important to know how wooden biomass is composed from these chemical constituents. This information can be beneficial for many reasons, for example in kraft pulping, in which penetration of cooking liquor into chips is one of the most important things to consider.

As can be seen in Figure 5, basic hierarchical structure of wood cells starts from cellulose molecules, which are further stabilized into 3,5 nm wide elementary fibrils by hydrogen

bonds between hydroxyl groups and interaction of oxygen atoms in adjacent cellulose molecules (Azizi Samir et al., 2005). These elementary fibrils are then aggregated into 5-30nm wide cellulose microfibrils, containing both crystalline and amorphous regions (Gustafsson et al., 2011) (Fernandes et al, 2011 as cited by Gibson L, 2012). Microfibril bundles of 100 nm width are composite formed from cellulose microfibrils encased in matrix composed of hemicellulose and lignin (Azizi Samir et al., 2005). Finally, lamellae of cells are formed from these cellulose macrofibrils (Gustafsson et al., 2011). Structure of wooden cells consists of different layers. These can be divided into primary layer, secondary layers, and in some cases, warty layer. The outermost space between cells is called middle lamella, and the innermost cavity in hollow cell is called lumen after death of cell, or protoplasm in case of young, live cells. From these cell walls, primary wall contains most of the lignin (Gibson, 2012) and secondary wall highest amount of cellulose (Bodig, J & Jayne, B, 1982 as cited by Gison, 2012). Secondary layer can be further divided into layers $S_1$, $S_2$ and $S_3$, which is also called the tertiary layer T, or in some species, warty layer W. From these layers, structural strength of wood can be highly attributed to layer $S_2$, which is responsible for most of the thickness of wood cell.

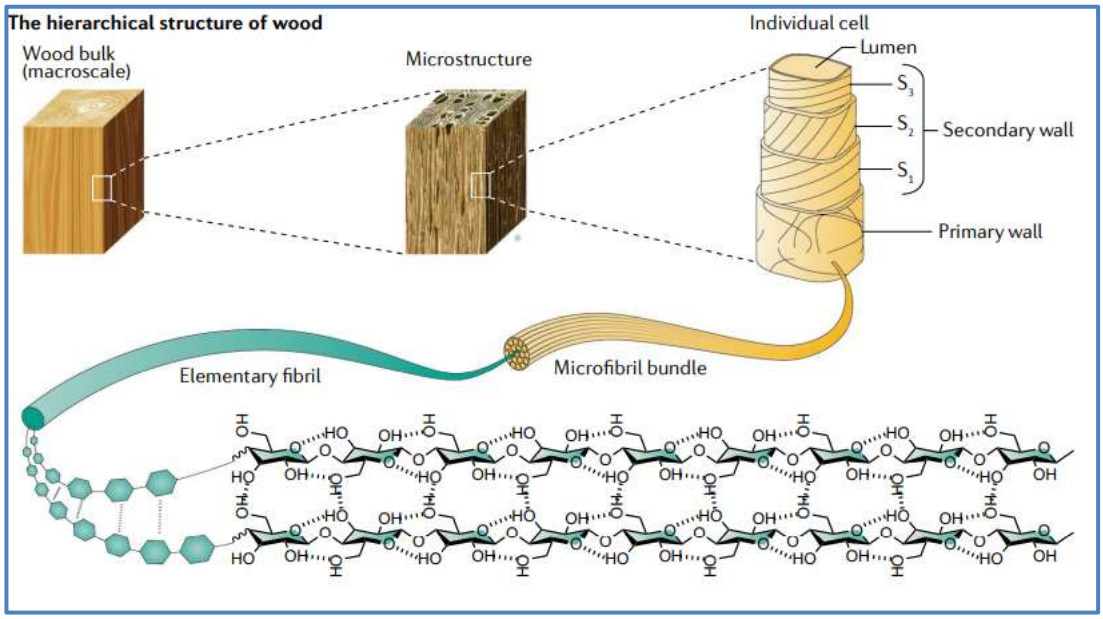


Figure 5: Hierarchical structure of wood (Modified from Chen et al., 2020)

Depending on species and type of tree, the structure of wood might have significant differences, even though basic structure of cells is quite similar. The most important one between softwoods and hardwoods is the difference between types of cells present. These cells can be roughly divided into long and thin prosenchyma cells with flattened edges,

and shorter, brick-like parenchyma cells (Gustafsson et al., 2011). Whereas softwoods have 90-95% prosenchyma cells called tracheids responsible for both structural strength and transportation of fluids, hardwood have different cells for these both tasks (Gibson, 2012) (Gustafsson et al., 2011). Hardwood cells responsible for conducting fluids are called vessels, which constitute about 30% of volume in hardwood xylem. For structural support, there are many kinds of fibre cells, about 55% of xylem volume. In softwoods, other cell types include ray tracheids (<5%), ray parenchyma cells (<10%), and epithelian parenchyma cells (<1%). In addition to fibres and vessels, hardwoods contain 15% of ray parenchyma cells, and <5% of longitudinal parenchyma cells. In case of pulping, longer tracheids of softwood pulp are responsible for longer fibres and thus better strength properties of pulp. With hardwoods, larger amount of short parenchyma cells are responsible for larger amounts of fines in pulp, which is usually considered negative feature (Gustafsson et al., 2011). Both softwood and hardwood species contain pits for conduction of water and nutrients through the tree. Because these pits have unique shape and orientation to each species, they can be used for identification of wood species. In addition, knowledge about pits of wood is beneficial for chemical pulping because they directly affect penetration of cooking liquor into chips (Gustafsson et al., 2011). Other structural elements of wood includes rays and resin canals which are present especially in softwood species (Gustafsson et al., 2011). Larger amounts of resin and other extractives in softwood requires additional pulping steps, which will be discussed more in following chapter about kraft pulping.

Concentration of wood constituents in different parts of wood is not constant, so it might be beneficial to know for example, how different parts of wooden biomass respond to chemical pulping. For example, reaction wood which is called compression wood in softwood and tension wood in hardwood, have different physical and chemical composition compared to wood in straight stem of a tree (Gustafsson et al., 2011). Compression wood usually contains higher amounts of lignin and other aromatic compounds which are harmful in chemical pulping (Gustafsson et al., 2011). In case of hardwood tension wood, pulping yield might be better than in normal wood, but strength properties of this pulp are usually worse (Gustafsson et al., 2011). In addition, bases of branches (called knots) are resinous and hard. This usually means they aren't pulped properly during cooking and are thus removed from pulp by screening (Gustafsson et al., 2011). Chemical and physical composition of heartwood and sapwood is also different. Heartwood contains more resins and other organic compounds than sapwood, and it has

higher density, which makes penetration of cooking liquor more difficult (Gustafsson et al., 2011). In addition, growth of wood differs between seasons. In spring, earlywood with thinner cell walls and larger lumens is formed for better transport of water and nutrients, and in summer, latewood with thicker cell walls for higher structural strength is formed.

### **2.1.5** Kraft pulp

As explained before in the first chapter, kraft process has several advantages, which have made it one of the dominant methods for chemical pulping in the world (Fernández-Rodríguez et al., 2019). Because this study utilizes kraft pulp as raw material for spinning of fibres, it is evident that basic principles of kraft process need to be explained for better understanding of phenomena regarding this study.

In kraft process, either softwood or hardwood raw material is first debarked, chipped, and screened for removal of fine material harmful to the process. These chips are fed to the digester and steamed for removal of excess air (Gustafsson et al., 2011).

Cooking of chips is conducted with mixture of strong alkaline solution, called cooking liquor. This solution contains pure white liquor, composed of mainly sodium hydroxide (NaOH) and sodium sulphite ($Na_2S$), and recycled black liquor, which in addition has dissolved lignin, extractives, and other fine components originating from earlier cooking of pulp. Cooking of chips starts in temperature of 80°C-100°C, after which it's quickly raised to 150°C-170°C, initiating the delignification process. Delignification process can be divided into three different phases: Initial delignification, bulk delignification, and residual delignification. In initial delignification, cooking liquor is still diffusing into chips. In this phase, the rate of delignification is still quite low, especially compared to relatively high degradation of carbohydrates. Only about 20-25% of lignin is dissolved in this phase (Gustafsson et al., 2011).

The first delignification step is followed by bulk delignification, in which the rate of delignification is at its highest. This step is responsible for removal of 70-80% of lignin in pulp. At the end of this phase, rate of delignification starts to decrease as amount of alkali in liquor starts to deplete (Gustafsson et al., 2011).

The final phase in delignification is called residual delignification. In the beginning of this phase, about 90% of total lignin of pulp has already been dissolved. In residual

delignification, selectivity of degradation rection towards lignin is very low, which might cause excessive degradation of polysaccharides and thus cause lowering of yield. In addition, depletion of cooking alkali might cause undesired recondensation of lignin on fibre surfaces. Because of these reasons, residual delignification step is usually kept relatively short (Gustafsson et al., 2011).

Delignification of softwood requires larger amounts of alkali due to higher amounts of lignin present in chips. Compared to eucalyptus pulp, yield from softwood is usually 15-25% lower. For this reason, it is common that production rate with hardwood pulp is about 20% higher than when running softwood (Shackford, 2003).

This main cooking reaction is followed by different process steps, depending on strength- and brightness requirements of pulp, and origin of raw material being utilized (Shackford, 2003). Because these subsequent process steps aren't as relevant for this study as cooking process, they won't be explained as thoroughly.

In case of paper with high brightness requirements, cooking is usually followed by oxygen delignification and bleaching steps. Other unit operations in kraft process include knotting and screening of pulp, concentration steps, and recycling of cooking liquor (Gustafsson et al., 2011).

Main difference between softwood pulp and hardwood pulp can be found in their hemicellulose composition, amount of extractives, amount of lignin, and fibre dimensions. Because chemical composition and physical aspects of softwood and hardwood pulps have quite significant differences, it must be taken in account for when designing fibre lines (Shackford, 2003). Variation in properties exists even within softwood and hardwood species, which is why pulps from specific plants like eucalyptus might be used instead of mixtures (Shackford, 2003). Even though softwood pulp has superior strength properties, opacity, smoothness, and bulk are better with hardwood pulp, which gives these both their own purposes in production of lignocellulosic materials (Shackford, 2003). Usually, hardwood pulps including eucalyptus pulp can be produced in softwood fibre lines, but not otherwise around due to higher requirements for screening, washing, and foam management with softwood pulp (Shackford, 2003). Because yield from softwood is significantly lower than from hardwood, cooking liquor from softwood contains more solid material, which might cause capacity problems in case of mill

designed for pulping of hardwood (Shackford, 2003). Additionally, because softwood has more lignin and lower brightness after cooking compared to hardwood pulp, higher amounts of bleaching chemicals is required afterwards, which might cause the amount of bleaching chemicals to be insufficient (Shackford, 2003). Lastly, washing and screening of softwood pulp is usually more difficult than hardwood due to flocculation of longer fibres (Shackford, 2003)

Whereas softwood contains mainly glucomannan, hardwood has higher amount of xylan. In case of eucalyptus pulp, amount of xylan is lower than with birch for example, but still twice the amount commonly present in softwood species (Shackford, 2003). Even after delignification, higher amounts of xylan remain compared to glucomannan. This can be beneficial regarding higher yield from pulping of hardwood, but on the other hand, xylan tends to degrade into hexuronic acid, which acts to consume bleaching chemicals and thus makes brightness of pulp harder to increase (Gustafsson et al., 2011). This negative aspect of hardwood pulp can be minimized by chemically preventing formation of hexuronic acid (Gustafsson et al., 2011), using xylanase for reduction of xylan content (Shackford, 2003) or by adding acidic stage to bleaching sequence (Shackford, 2003).

With hardwood, amount of extractives is usually in range of 3-10%, compared to 10-25% in softwood. Because amount of extractives in softwood is significantly higher, it requires additional process steps for foam management. Insufficient removal of this black liquor soap might for example, cause the coating of chips and thus inhibit the penetration of liquor into chips. On the other hand, pulping of softwood produces valuable by-products including tall-oil and turpentine, which can be sold for additional profit (Shackford, 2003).

As of physical properties of fibres, softwood has 3-4 times longer fibres than hardwood. For example, length of softwood fibres is about 3,5mm, whereas fibre length with *Eucalyptus globulus* is about 1,1mm. Width of fibres is also generally two times higher with softwood compared to hardwood. This difference in physical dimensions of fibres causes softwood pulp to have superior strength and better runnability in paper machine compared to hardwood pulp. Because of better strength, softwood pulp is often utilized in fortification in applications where durability is required. Even with weaker strength properties, hardwood pulp still has its uses though: Because it has higher light scattering coefficient, higher initial brightness after pulping, higher opacity, and higher smoothness,

hardwood pulp is used to improve optical properties of paper. In addition, smoothness of hardwood pulp makes it ideal material for hygienic products (Shackford, 2003).

### **2.1.6** Dissolving pulp

Dissolving pulp is a pulp grade with very high alpha-cellulose content, which is typically over 92% for pulp made with acid sulphite process, and over 94% for prehydrolysis kraft pulps (Sixta, 2006 as cited in Chen et al., 2020). From these processes, prehydrolysis kraft process accounted for 56% and acid sulphite process about 42% of production of dissolving pulp in 2014. Popularity of prehydrolysis kraft process has been steadily increasing through the years, because of advancements in prehydrolysis kraft technology (Chen et al., 2016; Sixta, 2006). Another defining factor of dissolving pulp is its very high purity: Hemicellulose content is usually between 3-6%, and there is only trace amounts of lignin and extractives left in pulp (Sixta, 2006 as cited in Chen et al., 2020).

Because of low yield and high operating costs, dissolving pulp is usually utilized for products with high requirements for purity. One example of this is the cuprammonium rayon, which requires dissolving pulp from cotton linters as raw material for highest possible purity (Sixta, 2006). Other products produced from dissolving pulps include regenerated films and fibres such as viscose, cellulose esters, and cellulose ethers (Sixta, 2006). From these products, especially viscose and lyocell fibres are of great importance, because production of cotton can’t keep up with increasing population of the word (Björquist et al., 2018). Dissolving pulp is typically made from either softwood species pine or spruce, or hardwood species such as eucalyptus or beech, which account for 85% of production of dissolving pulp. Only about 10% of dissolving pulp is produced from cotton linters, which is explained by high cost of operation (Sixta, 2006).

The basic principle in prehydrolysis kraft process is quite similar to regular process in kraft pulping, but with additional prehydrolysis step. Because hemicelluloses are resistant to alkaline conditions and prolonged cooking causes degradation of cellulose, regular kraft process is insufficient for production of high cellulose dissolving pulps. Even though alkaline conditions might dissolve hemicelluloses such as xylan, tendency for adsorption onto cellulose microfibrils makes its removal difficult. For this reason, acidic prehydrolysis step is introduced for removal of hemicelluloses from the pulp (Sixta, 2006).

In theory, prehydrolysis step can be conducted either by water in 160-180°C (Springer & Harris, 1982 as cited in Sixta, 2006), in sulfuric acid with concentration of 0,3-0,5% at 120-140°C (Rydholm, 1982; Springer, 1966; Springer, 1968 as cited in Sixta, 2006), or with hydrochloric acid with concentration of 20-30% at 40°C (Springer, 1966; Papadopoulos et al., 1983 as cited in Sixta, 2006). With water, auto-ionization causes acetyl groups to be cleaved from xylan, which leads to formation of acetic acid and further hydrolysis of xylans glycosidic bonds. With increasing amount of acetic acid, concentration of hydronium ions also increases, leading to further degradation of hemicelluloses (Gustafsson et al., 2011; Sixta, 2006).

In case of sulfuric acid $H_2SO_4$, ratio between sulfur and sodium might rise too high, which affects solubility of lignin, and thus causes precipitation of lignin on different surfaces, including wood chips (Sixta, 2006). This in turn makes following alkaline kraft process more difficult. Hydrochloric acid might cause problems with corrosion, which makes it also unideal choice of acid for prehydrolysis (Sixta, 2006). Water prehydrolysis on the other hand might be insufficient for more lignin containing softwoods and has been observed to cause formation of pitch-like compounds which will further hinder efficiency of process (Sixta, 2006). In addition, usage of water requires energy intensive steps for evaporation in recovery of cooking liquor (Sixta, 2006).

To overcome these problems, prehydrolysis is nowadays conducted with special technique utilizing steam hydrolysis, where pressure of reactor is kept high, and hydrolysis products are neutralized and flushed out of digester before kraft cooking by addition of hot white and black liquors. Because neutralization and flushing is conducted with sodium hydroxide and sodium sulfide, prehydrolysis can be followed immediately with kraft process (Sixta, 2006).

Another popular way for production of dissolving pulp is acidic sulphite process, which was briefly mentioned in introduction. Even though this process has drawbacks like higher amounts of environmental emissions and incompatibility with some species of wood (Gustafsson et al., 2011; Sixta, 2006), it produces dissolving pulp with higher yield, higher reactivity, and better bleachability (Sixta, 2006).

Sulphite pulping is quite versatile pulping process, which can be conducted with wide variety of different bases, and in large pH range of 1-13,5. In case of dissolving pulp, desired range of pH is between 1 and 3, which is considered acidic bisulfite pulping.

Basic principle of sulphite pulping includes usage of sulphite and bisulphite as cooking chemicals. These chemicals are bound to their respective cation, which is usually calcium, sodium, ammonium, or magnesium. Choice of cation depends on its solubility in desired pH range of process. With acid sulphite pulping, all the cations mentioned before can be used, but with anthraquinone based sulphite pulping in highly alkaline pH range of 9-13, only sodium can be used as cation (Gustafsson et al., 2011; Sixta, 2006).

Wood is debarked, chipped, and fed into the digester, where the cooking liquor containing active sulphite and bisulphite chemicals penetrates the chips. Heating of batch is conducted by heating the cooking liquor in external heat exchanger with heat from steam, which is circulated back into the digester. The cooking is continued until desired temperature depending on pH range is achieved, which in acidic process is around 125-140°C. At the end of cooking, gaseous sulfur dioxide $SO_2$ is released from the digester and led back into acid tower, where it's reacted with limestone (in case of calcium as base) for production of calcium bisulfate for use in following batches. After cooking, washing, screening, bleaching and drying of pulp is conducted (Gustafsson et al., 2011; Sixta, 2006). Depending on base, it might be possible to regenerate spent liquor. Magnesium sulphite for example can be regenerated with scrubbing system, but calcium sulphite goes to landfill after evaporation and incineration of spent cooking liquid. In addition, by-products of sulphite pulping can be utilized in production of valuable products such as lignosulphonates and vanillin (Gustafsson et al., 2011).

Main pathways for reactions of lignin in acid sulphite cooking are sulphonation, hydrolysis, and condensation reactions. From these three reactions, sulphonation and hydrolysis are responsible for delignification of pulp, whereas condensation is harmful reaction to the process. The purpose of sulphonation is to make lignin more hydrophilic for better solubilization to cooking liquid. Hydrolysis and breakage of linkages of lignin is strongly dependent on high pH though, which makes sulphonation the main delignification pathway in acidic sulphate pulping (Gustafsson et al., 2011). Last reaction with lignin, condensation, happens when bisulphite concentration is not sufficient. This can be result from, for example, poor impregnation of chips. Condensation of lignin

causes darkening of pulp, formation of shives, and in worst case destruction of pulp (Gustafsson et al., 2011).

Hemicelluloses are also dissolved in acidic sulphate pulping by hydrolysis of glycosidic linkages, whereas less accessible cellulose stays largely intact. Large amounts of by-products from sulphite pulping such as xylose and furfural originate from pentose-rich hardwood species, which increases economic feasibility of process (Gustafsson et al., 2011).

Dissolving pulp produced with either one of these techniques can be further processed for large variety of different products. In this study, manufacturing of dissolving pulp was introduced because production of most of regenerated fibres strongly depends on utilization of dissolving pulp as raw material.

### **2.1.7** Pre-treatments for reduction of hemicelluloses and improved polydispersity

The effect of different pre-treatments on hemicelluloses in kraft pulps have been studied, because they might cause some unwanted problems in process when utilizing kraft pulp as raw material for man-made fibres (Gehmayr et al., 2011), or undesired properties in fibres (X. Jiang et al., 2020). For this reason, kraft pulp usually undergoes some sort of modifications for reduction of hemicelluloses, and for improved polydispersity of pulp. These modifications can be divided into chemical treatments such as cold caustic extraction (CCE) (Arnoul-Jarriault et al., 2015) or dilute acid extraction (Brienzo & Rypstra, 2015), physical treatment such as steam explosion (Martino et al., 2017), or enzymatic treatment, in which hemicelluloses are cleaved with either xylanase or mannanase, or average molecular weight of cellulose is lowered with endoglucanase (Gehmayr et al., 2011).

In CCE, concentrated sodium hydroxide (NaOH) solution of 2-4M in temperature of 20-50°C is used for dissolution of hemicelluloses, especially xylan (Rydholm, 1965 as cited in Arnoul-Jarriault et al., 2015). In addition, crystalline structure of cellulose goes under changes, which is called mercerization. This causes cellulose to become inert towards derivatization, and causes collapsing of pore volume, which further contributes to hornification of pulp (Gehmayr et al., 2011). CCE has excellent results for removal of xylan but is less effective against glucomannan. When CCE might remove 90% of xylan

in pulp, only about 50% of glucomannan is removed (Arnoul-Jarriault et al., 2015). This makes CCE effective with hardwood pulps containing larger amounts of xylan and lower amounts of glucomannan but is not good enough when treating glucomannan rich softwood pulps (Arnoul-Jarriault et al., 2015). In addition, possible hornification of pulp is another reason to study other possible methods of pre-treatment.

In dilute acid extraction, wood chips are treated with sulfuric acid concentrations of 0,3-0,7% (v/v) in temperatures ranging from 120℃ to 140℃, for duration of 20 to 40 minutes (Brienzo & Rypstra, 2015). With dilute acid extraction, up to 60% of pulp xylan can be extracted, but usually lower amounts are removed due high impact to pulp yield (Brienzo & Rypstra, 2015). In addition, acid hydrolysis isn't very selective towards hemicellulose, which means it also causes degradation of cellulose (Brienzo & Rypstra, 2015).

When utilizing steam explosion for removal of hemicelluloses, wood chips are packed into sealed chamber together with high pressure steam in high temperature (Martino et al., 2017). After short time, release of pressure causes expansion of steam inside lignocellulosic matrix, thus separating fibres (Martino et al., 2017). In addition, acetyl groups of xylan cause autocatalysis with hydronium ions, further driving cleavage of hemicellulose-lignin bonds, and causing cleavage of hemicelluloses into soluble monosaccharides (Chen and Liu, 2007 as cited in Martino et al., 2017). With steam explosion, 27% of xylan can be dissolved with minimal losses to yield (Martino et al., 2017).

Enzymatic treatments offer more specific and gentle methods for lowering hemicellulose content and polydispersity of pulps. In this case, enzymes can be divided into hemicellulases such as xylanase and mannanase, or cellulases such as endoglucanase.

Xylanase acts by randomly cleaving xylan chain and is extremely selective towards xylan (Collins et al., 2005), removing up to 46% of pulp xylan (Gehmayr et al., 2011). There is also evidence of xylanase inhibiting redeposition of xylan back onto surfaces of fibres after kraft pulping (Gehmayr et al., 2011). In addition, xylanase might increase brightness of pulp by cleaving hemicellulose-lignin complexes, thus causing easier liberation and removal of lignin (Gehmayr et al., 2011). Like xylanase, mannanases are a class of enzymes specific to degradation of mannan -based polymers (Dawood & Ma, 2020).

Endoglucanase has no effect on hemicelluloses, but acts to degrade amorphous parts of cellulose fibrils, causing increased exposure of crystalline cellulose, increased swelling behavior, and reactivity of cellulose (Henriksson et al. 2005 as cited in Gehmayr et al., 2011) It has also been shown that endoglucanase tends to cleave loose ends from cellulose chains, thus causing reduction in average molecular weight (Mw) of pulp (Hilden et al. 2005 as cited in Gehmayr et al., 2011).

## 2.2 Production and properties of man-made fibres

### **2.2.1** Spinning techniques in general

Spinning of man-made fibres can be mainly divided into melt-spinning, and solvent spinning. From these, the solvent spinning can be further divided into dry-spinning, wet-spinning, or dry-jet wet-spinning. In addition, techniques such as electrospinning and spinning of fibres by utilizing interfacial complexation have been successfully studied (Greiner & Wendorff, 2007; K. Zhang & Liimatainen, 2018). The method for spinning of fibres is usually chosen by comparing different physical properties of raw material being utilized, such as solubility of polymer into solvents, melting point, and melting stability of the polymer (Lundahl et al., 2017). In addition, some techniques under development such as electrospinning (Greiner & Wendorff, 2007), or drawing of cellulose nanofibres by utilizing interfacial complexation (K. Zhang & Liimatainen, 2018) might provide additional benefits, such as addition of medical agents or metals into fibres, which can be utilized in production of wound dressings with additional healing properties (Greiner & Wendorff, 2007), or in production of flexible electronics (Razdan et al., 2009).

Melt spinning is a technique, which is usually utilized with thermoplastic materials derived from petrochemical sources, including polyester, polypropylene, or polyamide, for example (Lundahl et al., 2017). In melt spinning, molten dope is extruded through spinneret, and formation of fibre is initiated with cooling and solidifying of dope (Greiner & Wendorff, 2007). Because additional solvents with additional process steps aren't required, this process is relatively simple (Lundahl et al., 2017). Even so, modern society is shifting from usage of petroleum-based products to more sustainable choices such as cellulose-based fibres, which has driven the research for different kinds of processes utilizing bio-based materials.

In electrospinning, melt or polymer solution is extruded through a nozzle, which also acts as an electrode. In laboratory scale, counter electrode is positioned in distance of 10-25cm from the nozzle. On the way through electric field of 100-500 kV/m in a cone-shaped trajectory, melt solidifies (or solvent evaporates), and fibre is formed on the counter electrode (Greiner & Wendorff, 2007). This technique allows production of very thin filaments, which allow use of these fibres in many unique applications (Greiner & Wendorff, 2007).

When utilizing cellulose-based materials, fibres are usually produced by dissolution of cellulose into a proper solvent, and utilizing either dry-spinning technique such as one in production of cellulose acetate where solvent is evaporated from fibre after regeneration (Atlas, 1968), wet-spinning where solvent is precipitated into an antisolvent, or dry-jet wet spinning, in which air gap is utilized for better orientation of fibres, providing many physical advantages compared to traditional spinning processes, such as in production of viscose (Hauru et al., 2016; Lundahl et al., 2017).

### **2.2.2** Wet-spinning of viscose fibres

Because this study is continuation to production process of viscose, explanation about basic principles of its manufacturing process is of the essence for better understanding of production of man-made cellulose fibres in general.

Production of viscose rayon is a complex, multi-stage process which utilizes high purity dissolving pulp as raw material. Process starts with steeping of dissolving pulp, which is also known as alkalization or mercerization. In this step, alpha-cellulose of dissolving pulp is converted into alkali cellulose by reacting it with sodium hydroxide in alkali concentration of about 17-19%. In same step, traces of resins, soluble parts of pulp, and hemicelluloses are removed with excess NaOH -solution. In the beginning of this step, concentration of alpha-cellulose is about 87-98% depending on quality of dissolving pulp being processed (Atlas, 1968).

At this point, concentration of alkali cellulose is about 30-35%, with NaOH concentration of 15-17%. The steeping process is followed by shredding, in which pulp is made into small crumbs. In next step, these alkali cellulose crumbs are aged under controlled temperature and time, utilizing desired catalysts depending on desired properties of

process. The reason for this step is to lower the degree of polymerization with oxidative depolymerization, because degree of polymerization directly affects viscosity of solution, which is important for successful spinning of regenerated fibres (Atlas, 1968).

After aging, solubility of cellulose is increased by reacting it with carbon disulfide in a process step called xanthation (Shackford, 2003). In this step, reaction between cellulose and carbon bisulfide is conducted either in dry drum or in wet churn with solution of sodium hydroxide. In following dissolution step, formed cellulose xanthate slurry is forced through sections of dissolver together with NaOH solution. This produces viscous solution, which originally gave this fibre its name “Viscose” (Atlas, 1968). The spinning process is very sensitive to impurities which might cause clogging of spinnerets and air bubbles, which might cause breakage of fibre, so solution is then mixed for improved uniformity, filtered for impurities, and finally led to deaeration for removal of air bubbles (Atlas, 1968).

Because xanthation increases the viscosity of solution, last step before spinning is ripening or de-xanthation of solution, where viscosity of solution is lowered until desired spinnability is achieved. In this reaction, spontaneous decomposition of cellulose xanthate is caused by alkali saponification of undissociated xanthate groups (Ikumi Kagawa & Haruo Kobayashi, 1951).

Solution is pumped to spinning machine, where nozzle of pump is submerged in coagulating bath, consisting of sodium sulfate (10-28%), sulfuric acid (5-15%), and zinc sulfate (0,05-7%) (Woodings, 2003). When alkaline cellulose xanthate solution is pumped through spinneret with small openings into acidic coagulating bath, it causes regeneration of cellulose. The reaction starts by formation of skin, which slows down the regeneration of fibre core (Atlas, 1968). Because core of fibre is still gelatinous, stretching of fibre can be utilized for better orientation, resulting in fibre with better mechanical properties (Atlas, 1968). Formation of fibre can be fine-tuned with several process parameters, including temperature of coagulating bath, draw ratio between jet velocity and draw-off velocity, flow speed of coagulation bath, or additives such as zinc sulfate, which slows down formation of skin in drawing of fibre (Atlas, 1968; Woodings, 2003). Fibres are wound up and collected with a wheel made from plastic or glass called godet. After winding up, fibres are collected with spinning machine, and guided to further neutralizing, desulfuring, bleaching, finishing, and drying steps (Atlas, 1968). Finished

fibres are either ready for shipment to customers, or they can be further refined in the same production plant (Atlas, 1968).

### **2.2.3** Mechanical properties of regenerated fibres

The important mechanical properties of regenerated fibres are fibre tenacity, fibre elongation, and linear density. For determination of these properties of fibres, several analytically important parameters including stress, tensile strain, breaking load, initial modulus, and yield point of fibres must also be understood (Morton & Hearle, 1975).

When considering physical properties, the dimensions of fibre must be taken in account. For example, longer fibre has greater change for incidence of weak spots compared to shorter fibres, which is important to take in account for, because breaking load for individual fibre depends on its weakest point. Breaking load is directly proportional to the cross-sectional area of the fibre, so uniformity in fibre dimensions is desired. Longer fibres also exhibit larger values for elongation, which is another reason for standardized testing protocol for fibres produced (Morton & Hearle, 1975).

Stress of fibre is defined by load divided by cross-sectional area of the fibre and is expressed in either Newtons per square meter [$N/m^2$], or Pascals [Pa]. Because of large variation in thickness of even individual fibre, it's quite difficult to define cross-sectional area needed for this definition. Therefore it's more useful to utilize unit for linear density, called tex. The unit tex or dtex, depending on scale required for calculations, means the mass of 1000 meters of fibre for tex, or 10000 meters for dtex. When stress is defined with load per tex, it becomes specific stress, which is useful variable for comparison of different fibres (Morton & Hearle, 1975).

Tensile strain is also one of the most important variables regarding synthetic fibres. It's defined by elongation of fibre divided by its original length and is expressed in percentages (Morton & Hearle, 1975).

When studying fibres, their mechanical properties are usually presented in load-elongation curves. From these curves, it's possible to find values for elongation at break, strength (also called breaking load), initial modulus, and yield point. When comparing fibres, breaking load can be converted into tenacity with division by linear densities of fibres being compared (Morton & Hearle, 1975).

Breaking point of fibre can be found in point 3 at diagram in Figure 6. This point also defines breaking load of fibre which is the force required for fibre to break (point 1), and elongation at break (point 4). From this Figure, we can also find the initial modulus of fibre, which is the short part at the beginning of curve, ending in yield point (point 2).

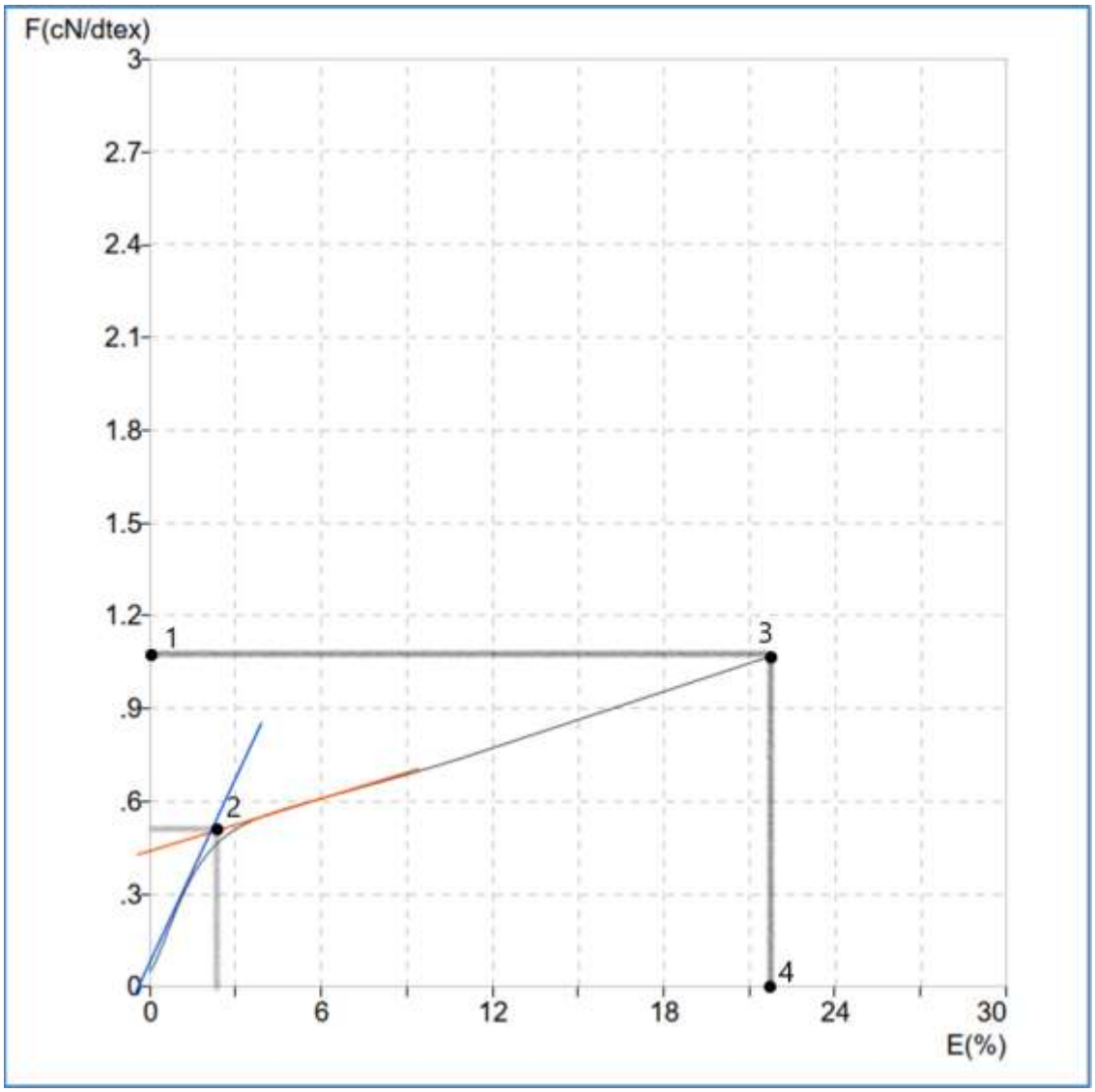


Figure 6: Load-elongation curve

Breaking point of fibre determines the absolute amount of steady force needed to break the fibre, which is important parameter to consider when fibre is under constant stress, in a rope for example. It might also be important to know the breaking elongation of fibre, if end product might be exposed to frequent stretching, which might be the case in clothing, for example. For same reason, yield point of fibre is also useful to know, because it determines the force and elongation after which the elastic behavior of fibre is irreversibly reduced. After this point, elongation of fibre becomes suddenly noticeably

easier. Last physical property to consider might be the work of rupture or toughness of fibre, which is determined by the area under load-elongation curve. This property of fibre tells us how much energy is required for breaking the fibre, which is usually considered when the end-product might be exposed to sudden, large amounts of force (Morton & Hearle, 1975).

It is also beneficial to notice, that the properties mentioned before should all be considered when selecting or developing fibre for certain type of stress. Rope for example, should be able to withstand both steady forces, but also sudden impulses without breaking. On the other hand, easy elongation of rope might be useful in some applications, but with towing rope it might be harmful (Morton & Hearle, 1975).

### **2.2.4** Physical properties of fibres

As important it is to understand mechanical properties of fibres, it is even more important to know what causes differences between those properties. Physical features of fibres can be attributed to properties such as ratio of amorphous and crystalline regions in cellulose, degree of orientation of cellulose molecules, and molecular weight distribution of pulp utilized in production of these fibres (Atlas, 1968).

As explained before, natural cellulose contains both amorphous, and crystalline regions (Figure 7). Proportions of these regions vary between celluloses derived from different sources, which explains their different mechanical and chemical behavior. For example, cellulose with more amorphous regions has better moisture absorption capabilities than more crystalline specimen but is also more susceptible to chemical modifications (Mark, 1940 and Hermans, 1941 as cited in Atlas, 1968). Amorphous regions can also be used as explanation for stretching behavior of fibre, whereas crystallinity of fibre is often associated with higher tensile strength (Atlas, 1968).

Degree of orientation is property of the less ordered regions of fibre, and it has significant effect on uniformity and mechanical properties of fibre, mainly flexibility, extensibility, elasticity, and tensile strength (Atlas, 1968). Alignment of fibre components is usually achieved by stretching of fibre during drawing, so higher draw ratios usually result in mechanically superior fibres. Proper coagulation conditions have to be taken in account though, because inadequate coagulation might result in so called “skin-core” structure

(Morehead and Sisson, 1945 as cited in Atlas, 1968), which might cause weak, telescope-like stretching (Hauru et al., 2016). With increasing alignment of fibre components along the fibre axis, the dimensions of fibre will become more uniform and thus the mechanical stress caused on fibre will be distributed more evenly, improving mechanical properties of fibre (Atlas, 1968). Of course, possibility to achieve high draw ratios depends on physical properties of dope, which is affected mainly through molecular weight distribution of cellulose being processed, and viscosity it causes on the dope (Atlas, 1968).

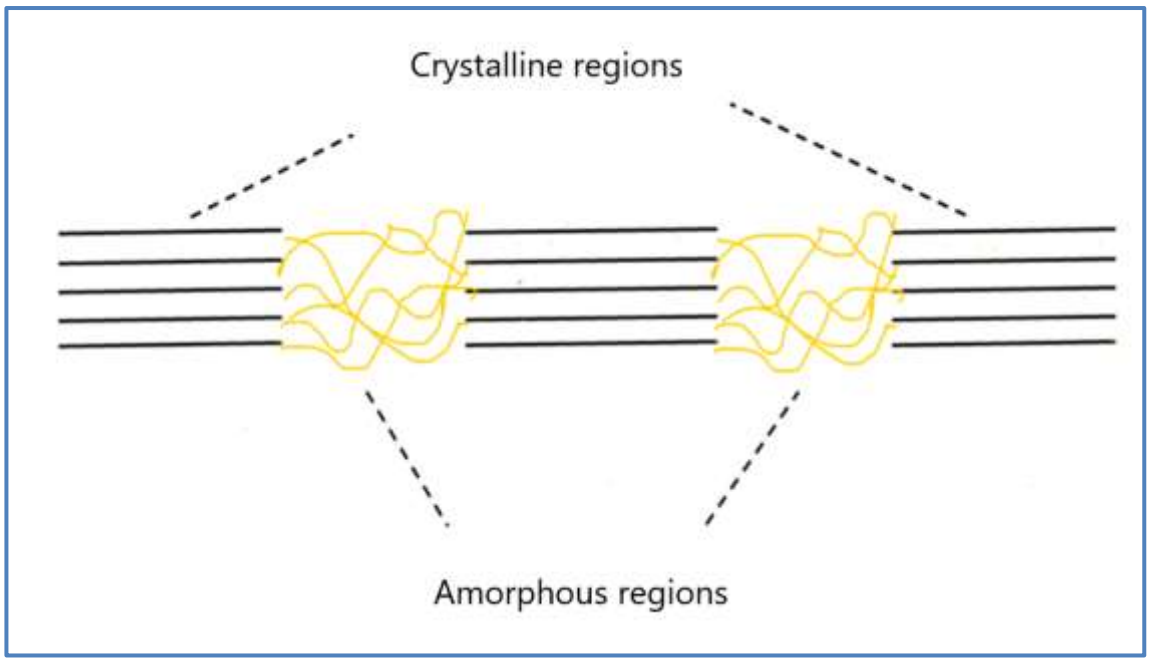


Figure 7: Structure of cellulose fibrils (Modified from Rajinipriya et al., 2018)

The crystallinity of fibre is caused by active groups present in cellulose molecules. These active groups have tendency to form intermolecular linkages such as hydrogen bonds, which cause the aggregation of polymer molecules and formation of regular, crystalline structure (Atlas, 1968). Degree of crystallinity has been shown to improve tensile strengths of fibres (Atlas, 1968), but also to adversely affect elongation properties of fibres, which are attributed to amount of amorphous regions of cellulose (Ward, 1950 as cited in Atlas, 1968)

Because pulp consists of different components, it's only natural that those components have varying molecular weights and degrees of polymerization. This variation is called the molecular weight distribution, which explains the relative percentages of components with different molecular weights. One of the most important parameters in spinning of

fibres is viscosity of the dope, which is directly affected by average molecular weight of the pulp being used (Atlas, 1968). Higher amounts of heavy molecules with larger degrees of polymerization cause higher viscosity, which is known to cause problems in spinning of fibres. On the other hand, too low average molecular weight might also cause poor fibre properties due to amount of short polymers in solution being too high (Atlas, 1968). It has been observed that tensile properties could be diminished with degrees of polymerizations as low as <300-500 DP with natural fibres (Staudinger et al., 1937 as cited in Atlas, 1968) or <100-150 DP with regenerated fibres (Staudinger, 1937 as cited in Atlas, 1968). The reason for this difference between natural and artificial fibres has been suggested to be the difference in morphological structure of fibres (Atlas, 1968). Effect of short, lower molecular weight polymers has been speculated to cause decline of fibrillar properties by having less molecular interlinks and more molecular breaks morphological units of cellulose. This is the case especially in less ordered, amorphous regions, where molecular breaks are not compensated with as many hydrogen bonds as in crystalline regions (Atlas, 1968).

## 2.3 Ionic liquids with cellulose

There are massive amounts of possible structures and uses for ionic liquids. Because the subject of this study is focused on cellulose and there is vast amount of information available about ionic liquids, this chapter will be limited to basic information about ionic liquids, and their use with lignocellulosic material.

Ionic liquids are low melting point salts, which are built from anion core, cation core, and different substituents, depending on intended use of said ionic liquid. Because many different options for cores and substituents for both cations and anions exist, there might be over million different permutations with different properties (Rieland & Love, 2020). For this reason, ionic liquids are also known as “Designer solvents” (Moniruzzaman & Ono, 2013). Ionic liquids are defined by their melting point, which must be below boiling point of water, and often ionic liquids might be liquid even at room temperature (el Seoud et al., 2007). Other properties of ionic liquids include their low steam pressure, non-volatility, and their chemical and thermal stability (el Seoud et al., 2007). These properties make ionic liquids relatively safe chemicals to use, and their stability is beneficial for recycling of said solvents, which makes their use potentially economical and relatively “green” (el Seoud et al., 2007). Ionic liquids are usually thermally stable in temperatures

under 200°C, which is beneficial in processing of biomolecules like cellulose, which is normally solubilized and functionalized in temperatures as high as 150 °C (el Seoud et al., 2007). As a matter of fact, this green aspect of ionic liquids has been one of the main driving forces behind the research of better and cheaper ionic liquids (el Seoud et al., 2007). Ionic liquids are still quite expensive and labor intensive to produce, for it might take up to 120 hours to synthesize some ionic liquids (el Seoud et al., 2007). Nevertheless, chemical producers have started to show interest on ionic liquids and nowadays they can be produced for as low as 4$ per gram of liquid, which makes their industrial utilization feasible (Rieland & Love, 2020).

Utilization of ionic liquids to solubilize cellulose can be attributed to the fact that cellulose is insoluble in water, so some kind of chemical treatment is required for solubilization (Rieland & Love, 2020). With suitable solvent (like ionic liquid), process can be quite simple and effective. Solubilization of cellulose in ionic liquid is mainly caused by hydrogen bonding between anion of ionic liquid, and hydroxyl groups of cellulose (Singh et al., 2009). Furthermore, cations of ionic liquid further contribute to electrostatic interactions inside the solution, which further drives solubilization of cellulose (Badgujar & Bhanage, 2015). Solutions with up to 20w% of cellulose can be produced with ionic liquids (Rieland & Love, 2020). Because viscosity of ionic liquid steadily increases with amount of cellulose dissolved, concentrations as high as 20w% might not be spinnable because of their extremely high viscosity (Rieland & Love, 2020). In addition to poor spinnability, too high viscosity can disrupt swelling and dissolution of cellulose (el Seoud et al., 2007) (Kuzmina et al., 2017). It has been observed that average molecular weight of cellulosic material has great effect on viscosity when dissolved into ionic liquid (Kuzmina et al., 2017). Because viscosity of the solution is one of the most important process parameters for spinnability, it must be optimized: Viscosity of solution must be low enough to allow extrusion through spinneret, but high enough to allow drawing of fibres (Rieland & Love, 2020). Viscosity of solution is also important for economic aspects of process, because higher viscosity causes higher energy expenditure in mass transfer (Rieland & Love, 2020).

It has been observed that ionic liquids can dissolve cellulose in temperatures as low as room temperature (el Seoud et al., 2007). Because speed of dissolution is faster in higher temperatures and ionic liquids have low vapor pressure, it is wise to use higher temperatures for dissolution. Viscosity is also strongly dependent on temperature of

liquids, which helps with problems associated with high viscosity mentioned before. This is also one of the advantages of ionic liquids comparing to traditional solvents, because traditional solvents might cause degradation off cellulose in temperatures as low as 90 °C, whereas ionic liquids are often thermally stable in temperatures as high as 200 °C (el Seoud et al., 2007).

One of the more serious drawbacks of ionic liquids is their sensitivity to even small amounts of water: Because water has tendency to form hydrogen bonds with anions of ionic liquid, water drastically lowers solubilization effectiveness of solvent (Singh et al., 2009). Nevertheless, basic principle of regeneration of cellulose from ionic liquid is based on the fact, that water has strong tendency to form hydrogen bonds with anion of ionic liquid. For this reason, cellulose can be regenerated from solution of ionic liquid just by drawing the solution through liquid which tends to form hydrogen bonds, like ethanol, acetone, or in case of this study, water (el Seoud et al., 2007).

Rheology of ionic liquids is affected by many things, including temperature (Smith et al., 2013), pressure (Pensado et al., 2008), amount of water (Burrell et al., 2010), amount of dissolved cellulose (Endo et al., 2016), and molecular weight of polymer (Amann et al., 2012). Because ionic liquids are very sensitive towards contaminants and especially water, information about rheology of ionic liquids varies (Rieland & Love, 2020). Most ionic liquids usually behave Newtonian above their melting point, but under higher temperatures and high shear rates, shear thinning is usual (Rieland & Love, 2020)

In continuous industrial process, it would be economical to recycle ionic liquid. This could be achieved with distillation, LLE (liquid-liquid extraction), membrane-based methods, induced phase separation, or adsorption (Mai, Ahn, & Koo, 2014). Because Ionic liquids are water soluble and may undergo degradation reactions in water commonly used as coagulation medium to solidify cellulose, it is often difficult to separate used ionic liquid from bath. This results in higher reagent or energy expenses, which both lower economic viability of process (Rieland & Love, 2020). Nevertheless, some studies have shown that recycling of solvent is possible (Halder et al., 2019; Mai, Ahn, Bae, et al., 2014).

In continuous process, some ionic liquid continuously diffuses into coagulating bath, which means that bath composition will change during time, if recycling of solvent isn’t

fast enough. For this reason, studies have also been conducted with coagulating bath including set amounts of ionic liquid. In study conducted by (Guizani et al., 2021), it was observed that fibres could be spun in bath containing as high as 30w% of ionic liquid, without significant losses in fibre properties. It was shown that bath containing ionic liquid actually increased tenacity of produced fibres, but affected elongation negatively, which was attributed to kinetics of coagulation and regeneration (Guizani et al., 2021)

### **2.3.1** Dry-jet wet-spinning

Dry jet wet spinning is a technique, where cellulose-containing solution is extruded through a spinneret and small air gap into a coagulating bath consisting of water, where fibre is formed and then spun onto a rotating cylinder called godet (Hauru et al., 2016). The product called Lyocell is the best example and only commercial process utilizing dry-jet wet spinning in production of regenerated cellulose fibres. In case of Lyocell, pulp is dissolved into organic solvent, such as N-methylmorpholine N-oxide (NMMO) without derivatization step present in production of viscose (Lundahl et al., 2017). Stretching of fibre is achieved in small air gap for better orientation and crystallization, and thus improved physical properties of fibres (Hauru et al., 2016). This stretching is produced by positive draw ratio between jet velocity and take-up velocity, which be further discussed in following chapter about properties of fibres (Hauru et al., 2016).

### **2.3.2** Important process parameters

Several parameters affect the mechanical properties of produced fibre. These include viscosity of dope, molecular weight distribution of cellulose (MWD), aspect ratio of the spinneret, draw ratio (DR), and residence time in coagulating bath (Asaadi et al., 2016). In addition to these important process parameters, things such as the amount of lignin and hemicellulose in dope can disrupt the crystallinity of formed fibre, which in turn will lower the strength and elastic modulus (Ma et al., 2016) of produced fibres with amounts under 20w% (Sun et al., 2011). Amount of air bubbles must also be minimized, because even small bubbles can disrupt the formation of fibres.

From these process parameters, viscosity of the dope is the most important thing to consider, for reasons which were already explained before. Draw ratio is the ratio between extrusion velocity in spinneret and take-up velocity of rotating cylinder, calculated with a formula $D = V_L/V_0$ (Asaadi et al., 2016). Higher draw ratios increase orientation of

cellulose molecules and crystallinity in the manufactured fibre, thus increasing its mechanical properties (Hauru et al., 2016) (Guizani et al., 2021). Higher DR is also one indicator of successful process, together with spinning time without breakage of fibre (Guizani et al., 2021).

Residence time of fibre in coagulating bath is also one of the most important process parameters, because regeneration of cellulose fibre is dependent on diffusion of water onto surface of fibre, and at the same time, diffusion of the ionic liquid from surface of fibre to regeneration bath (Hauru et al., 2016). If residence time is not sufficient, fibre might form kind of "Core-skin" -structure, in which skin of the fibre hardens while core is still soft, causing stretching of the core and formation of weak, telescope -like structure (Hauru et al., 2016)

It has been observed that molecular weight distribution of cellulose affects strength and elastic modulus of fibres (Sun et al., 2011). When average molecule weight and degree of polymerization of cellulose are too high, viscosity of solution might be too high for spinning of fibres. Too low molecular weight with narrow MWD might not allow sufficient tangling of cellulose chains to produce strong fibres (Hauru et al., 2016), whereas with too high molecular weight, too much tangling might cause viscosity to become too high (Asaadi et al., 2016). For these reasons, finding proper MWD is a matter which needs to be optimized for the best quality and processability of fibres.

Aspect ratio of spinneret has also been observed to affect strength of fibres. Aspect ratio is calculated with formula AR = (L/D), where L is the length of capillary, and D is the diameter. Increasing aspect ratio has been shown to increase tenacity and strength of fibres, probably by increasing crystallinity and orientation of cellulose chains (Guizani et al., 2021).

# 3 MATERIALS AND METHODS

## 3.1 Materials

Both softwood-, and hardwood kraft pulp samples were obtained from VTT's research center in Otaniemi, Espoo, where molecular weight distributions of different cellulose samples were adjusted into desired values. Ionic liquid mTBNH-OAc was obtained from research center of university of Helsinki in Kumpula, Helsinki.

### **3.1.1** Pulp samples

The pulp samples were pre-treated to adjust the average molecular weight (Mw) of the pulps to desired level. The target level for the dissolution and especially for the fibre spinning was agreed to be 430-450 ml/g measured as intrinsic viscosity (Scan μ). The pre-treatments were mechano-enzymatic treatments at high consistency (Spönla, 2020), acid treatment with sulphuric acid ($H_2SO_4$), steam explosion, and cold alkali extraction (CCE). The mechano-enzymatic treatments were carried out in a farinograph mixer (Brabender, Germany). Enzymes, commercial endoglucanase (Fibercare R, Novozymes, Denmark) alone and in a combination with hemicellulases, mannanase (Tr Man5A) and xylanase (Tr Xyn11A), were dosed base on their protein content as indicated in Table 1 (Spönla, 2020).

Table 1: Properties and treatments of pulp samples

| Sample | Scan μ (ml/g) | Mw (kDa) | Endoglucanase ( mg/g) | Hemicellulase (mg/g) | Other | Yield (%) |
|---|---|---|---|---|---|---|
| SW1 | 450 | 250,5 | 0,02 | 0 | No | 98 |
| SW2 | 430 | 241,8 | 0,0175 | 0,1 xyl + 0,1 man | No | 99 |
| SW3 | 440 | 149 | 0 | 0 | Acid | 99 |
| SW4 | 540 | 293 | 0 | 0 | Acid | 99,6 |
| SW5 | 450 | 265,1 | 0,02 | 0 | CCE | 96 |
| HW1 | 430 | 224,7 | 0,57 | 0 | No | 98,6 |
| HW2 | 430 | 224,5 | 0,06 | 0,1 Xyl | No | 92 |
| HW3 | 460 | 225 | 0,028 | 0 | CCE | 84 |
| HW4 | 450 | 233,4 | 0 | 0 | S.Exp | 92 |

Softwood pulp was treated with $H_2SO_4$ at 90°C with two different concentrations for durations of 45 and 60 minutes.

Cold alkali extraction was done for hardwood pulp and endoglucanase treated softwood pulp. The pulps were treated at 30°C for 30 min at 10% (w/v) pulp consistency using 70 g/L NaOH concentration and 200 rpm mixing. Conditions for the treatment were modified from (Gehmayr et al., 2011). Cold alkali extracted hardwood sample was further treated with endoglucanase.

Steam explosion of hardwood pulp sample was carried out by treating the pulp with hot steam (195 °C) for 12 minutes in a pressure reactor using a previously published protocol (Niemi et al., 2017).

The intrinsic viscosity of the pulp samples were determined as a SCAN viscosity according to ISO 5351-1. The molecular weights of the pulps were measured with size exclusion chromatography after dissolving the pulps in 8% LiCl/DMAc. Yield losses of hardwood pulp samples were measured as dissolved sugars from the filtrate by using dinitrosalicyclic acid assay for reducing sugars. Yield losses of softwood pulp samples were analysed by hydrolysing the filtrate into monomeric sugars and by carrying out compositional analysis with liquid chromatography (Spönla, 2020).

### **3.1.2** Solvent

Superbase ionic liquid [mTBNH][OAc] (5-methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate) was synthesized at university of Helsinki.

Solvent has melting point of ~15°C, with hydrolytic stability of <1% degradation products at 80°C, increasing to <6% at 130°C, when concentration of IL in water solution is 50wt%. Solvent was stored in fridge for longer periods between testing, or in room temperature covered in aluminum foil when testing happened daily. Melting of ionic liquid was conducted after refrigeration with hot water bath

## 3.2 Methods

### **3.2.1** Optimization of water activation protocol

Three different methods for water activation were tried with cellulose sample HW1, endoglucanase treated softwood pulp. These were named method A, method B, and method C. All dilutions were conducted with addition of cold, deionized water.


Figure 8: Flow chart of water activation protocols

Method A, in which dry matter content (DMC) of pulp sample was first adjusted to 50wt% on a petri dish, and furthermore into 20wt%, because swelling of pulp wasn't deemed homogenous enough. With method B, pulp was diluted into very low consistency (under 1wt%) in decanter glass. As for method C, treatment of pulp was similar to sample A, with difference of mixing the pulp and water inside a kneader (Figure 9). Sample C was further divided into two samples: HW1C1 and HW1C2. Difference between these samples was similar to samples A and B: As HW1C1 was mixed in large amount of water in consistency of about 1wt%, sample HW1C2 was dried on a petri dish after addition of

water. All the samples were ultimately dried in draft cabinet into DMC of 50wt% and kept in fridge for approximately three days before dissolution trials. Flow chart of different water activation protocols can be seen in Figure 8.

Solutions of 10 wt% were produced by dissolving pulp samples into ionic liquid with an overhead mixer and placed into vacuum oven (Salvis lab, Switzerland) for 24 hours in temperature of 85°C and pressure of 550mbar. After heat treatment, dissolution success of samples was inspected by eye, and confirmed with an optical microscope (Leitz diaplan type 020-437.035, Germany) with digital camera (Euromex TL20614, Netherlands) and imaging software (Euromex imagefocus 4, Netherlands).

Figure 9: Kneader used in water activation of pulp

**3.2.2** Water activation of cellulose samples

Dry pulp samples were weighed with laboratory scale (Mettler PJ3600 delta range, USA). Water activation was conducted at room temperature with three different methods, which determined whether samples were mixed in two steps with kneader (IKA-werke duplex kneter MKD 0,6 H60, Germany), and an overhead mixer (Heidolph RZR 2021, Germany), or in one step with an overhead mixer. During mixing, pulp consistency was adjusted to low value of around 1 wt% with cold deionized water. Water activated samples were dried in draft cabinets until formation of dry cellulose sheets close to target dry matter content of 20 wt% or 50 wt%, after which they were torn into decanter glass, and weighed with laboratory scale. Water contents were adjusted into 50% by addition of

cold deionized water, and samples were put into fridge for moisture to even out in the samples.

### **3.2.3** Dissolution of dried cellulose samples

Total of nine different pulp samples with five different pre-treatments were received from which five were softwood kraft pulp, and remaining four were hardwood kraft pulp originating from *Eucalyptus globulus*. Samples were treated both enzymatically and chemically for reduction of hemicellulose contents, for lowering the degree of polymerization (Dp), and for improvement to overall molecular weight distribution (MWD) for improved viscosity for better spinnability of dopes. Dissolution trials began with solutions of 10wt%, which was lowered for adjustment of viscosity during trials.

Figure 10: Mixing of pulp into ionic liquid

Ionic liquid and air-dried cellulose samples of 92 wt% to 95 wt% were weighed with laboratory scale for preparation of 10 wt% solutions with concentrations ranging from

10wt% to 5wt%. Pulp samples were mixed into ionic liquid at room temperature, with an overhead mixer (Figure 10) for about 5 minutes. Afterwards mixtures of pulp and ionic liquid were placed into an oven (Memmert ufe 400, Germany) for duration of approximately one hour. Success of dissolution was determined with an optical microscope.

### **3.2.4** Dissolution and gas removal from water activated samples

Basic procedure for solvation of pulp samples into ionic liquid was conducted by measuring set amounts of pulp and ionic liquid with laboratory scale. Pulps were mixed into ionic liquid with an overhead mixer in room temperature for five minutes, resulting in thick. viscous slurry which can be seen in Figure 11.

Figure 11: Well homogenized pulp samples

Solvation was continued in temperatures ranging from 85°C to 95°C, and vacuum of 300 to 500 kPa inside either oven, vacuum oven, or custom-made vacuum reservoir with glycol bath for temperature control, depending on amount of gas bubbles present (Figure 12), and availability of desired equipment at the moment of solvation. Because dissolved

pulp had DMC of 50wt%, temperature and pressure of system was selected for boiling point of water, which is 80°C in pressure of 540mbar to remove residual water from the solution. Because gas removal efficiency is dependent on temperature, pressure, and viscosity of solution, residence times for samples inside heating equipment varied between 24 to 125 hours. Different pulp samples are listed in Table 1, with information about scan viscosities, molecular weights, pre-treatments, and yields from pre-treatments. In addition to pre-treated pulp samples, sample of dissolving pulp was tested for reference.

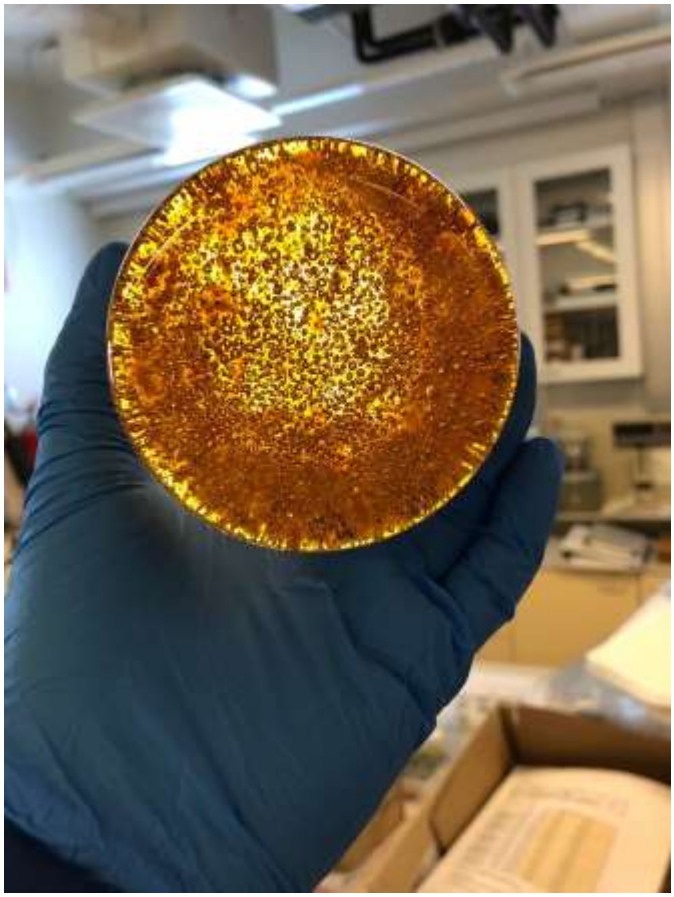

Figure 12: Air bubbles after dissolution

**3.2.5** Spinning trials

Dopes of 50-60g were pre-heated to reduce viscosity for better spinnability. This was done with either oven, vacuum oven, syringe heater (New era pump systems inc heater-kit-5sp, USA), or vacuum reservoir. Samples were packed in either plastic 50ml, or steel 200ml syringe (New era pump systems inc, USA), and extruded through spinneret with eight 50µm holes by using mechanical pump (Kf technology NE-8000, Italy). Fibres were

guided through coagulating bath with two guides, resulting in regeneration length of 0,62m before collection with custom-made laboratory-scale spinning equipment, with adjustable speed for godet (Figure 13). Circumference of godet was measured, and speed corresponding to frequency displayed by machine was calculated from three displayed frequencies (300, 1500, and 2700). By utilizing this data, conversion tool was built with Microsoft office excel to determine frequency required for desired speed, which was set between 0,63 m/s and 4,31 m/s, depending on extrusion speed of pump and spinnability of fibres. Fibres were left to soak in room temperature deionized water for approximately four days for removal of ionic liquid, after which they were washed with ethanol (Figure 14) and dried for approximately three days (Figure 15). Fibres were finally examined with optical microscope and sent for further mechanical testing.

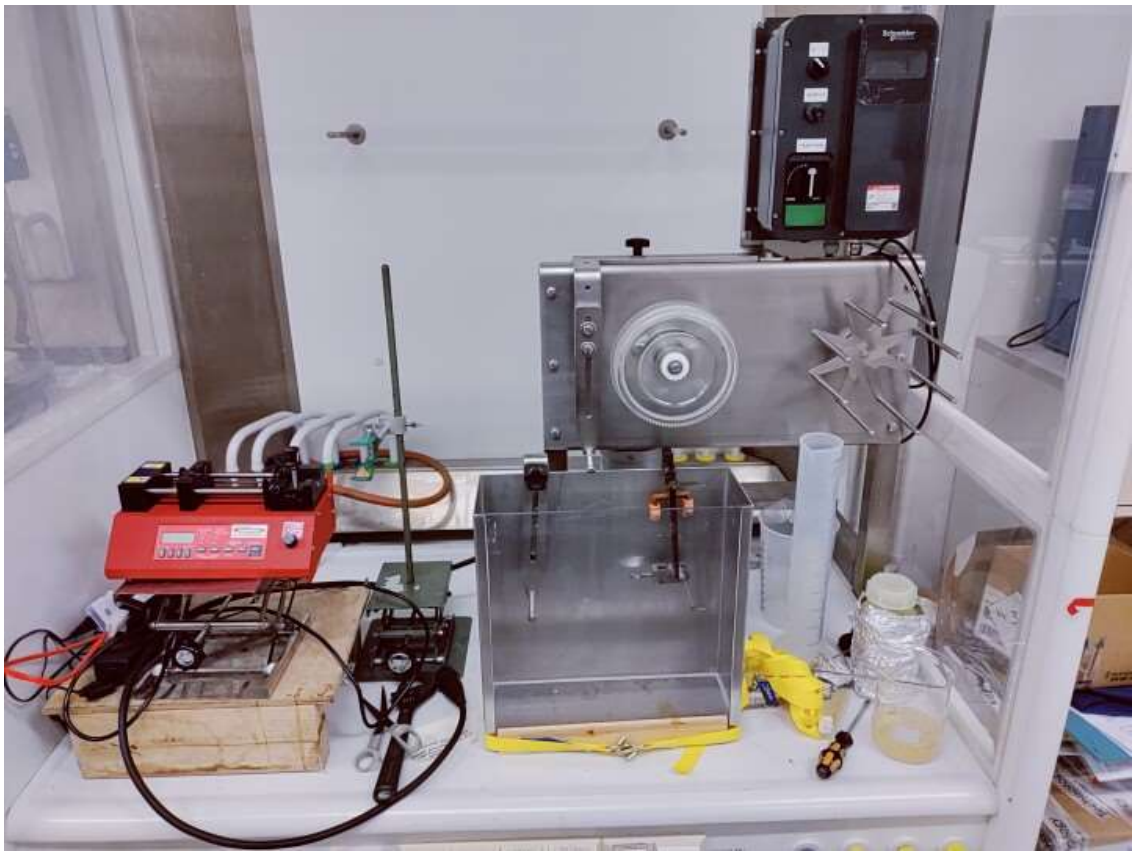

Figure 13: Spinning equipment

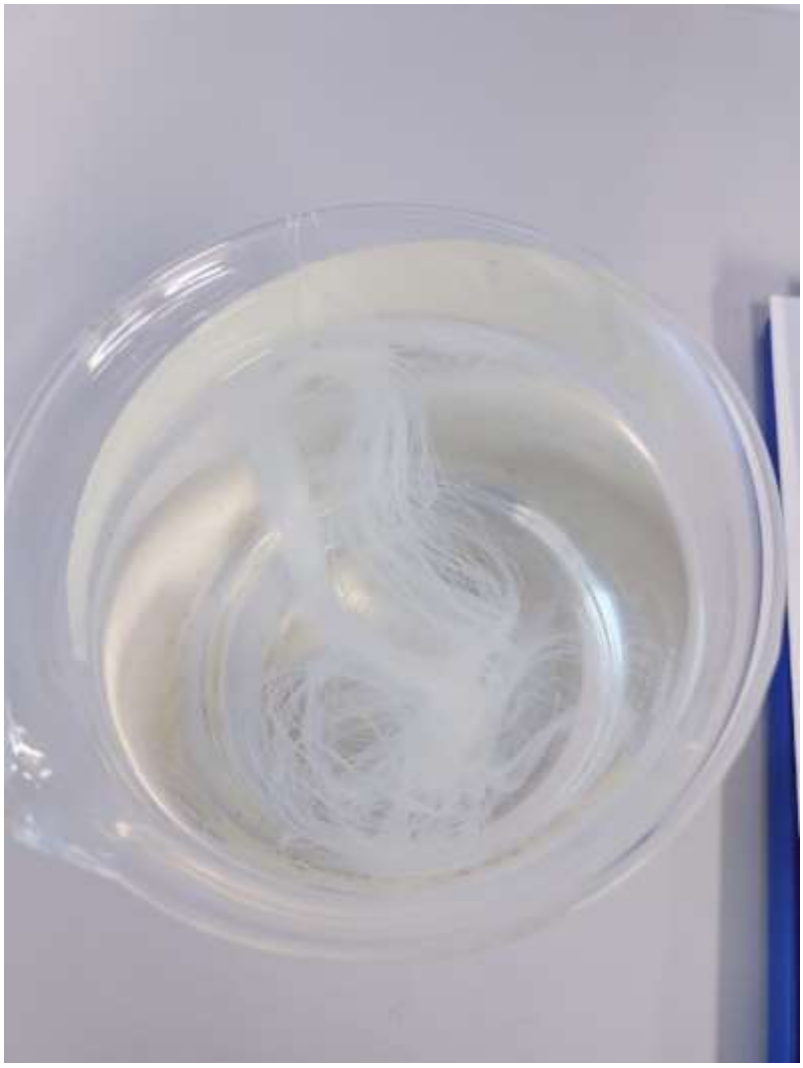

Figure 14: Washing of fibres

Figure 15: Fibres being dried

### **3.2.6** Analysis of samples

Samples were examined with optical microscope (Figure 16) for solubilization of fibres after mixing and after heat treatment, and surface structure of fibres after spinning and drying.

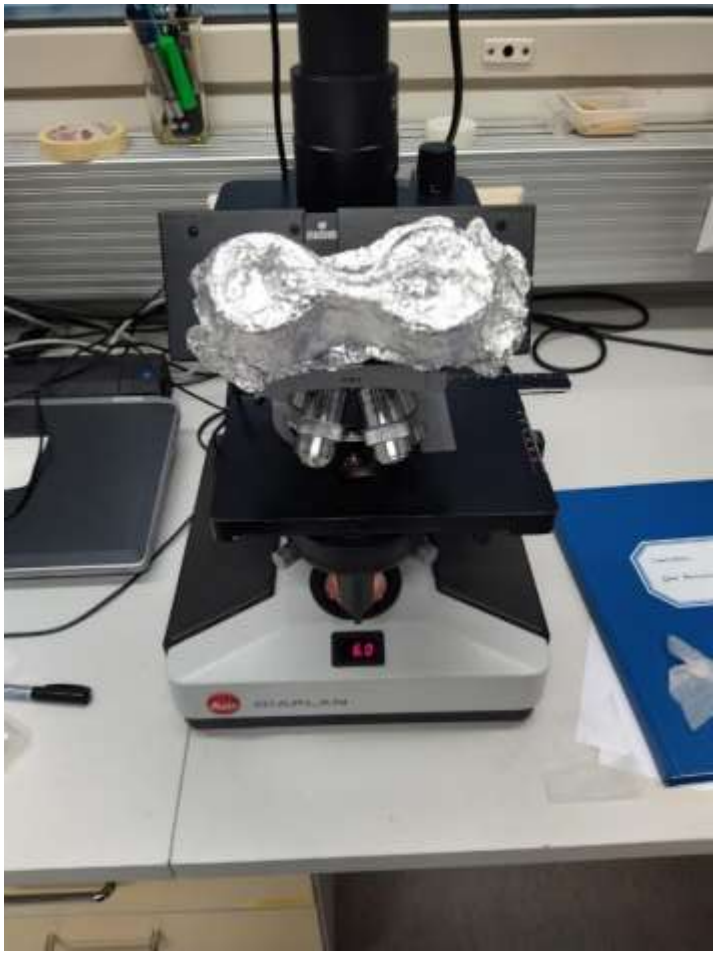

Figure 16: Microscope used for analysis of samples

Mechanical testing of fibres for elongation, maximum force, tenacity, linear density, and initial modulus was conducted with FAVIMAT+ fibre tester (Favimat+, Germany) by using load cell of 210 cN, and gauge length of 20mm. Test speed varied, being standard speed of 5,0 mm/min in linear density tests, and 20mm/min in tensile test. With linear density tests, pretension was 0,10 cN/dtex differing from pretension of 0,05 cN/dtex with tensile tests. Testing of fibres was conducted ten times for every series of fibres from same sample, and average results were calculated. The results are collected in Table 7, which can be found in chapter 4.3. In addition, results for commercial fibres have also been listed in Table mentioned before for possibility of comparing fibre properties.

# 4 RESULTS AND DISCUSSION

## 4.1 Effect of pre-treatments on pulp samples

Depending on severity and selectivity of pre-treatment methods, different pulp samples had some very big differences in their yields, resulting in yield losses ranging from 0,4% of acid treated sample SW4, to 16,2% of sample HW3 treated with endoglucanase and CCE (Table 2). Like explained in chapter 2.1.7, different pre-treatment methods have different effects on wood constituents. For example, endoglucanase only targets cellulose, which explains very modest yield losses in samples treated only with endoglucanase. Other methods such as CCE are very effective against xylan, which might cause huge losses in yield, especially when coupled with cellulose dissolving endoglucanase treatment.

Table 2: Causes of yield losses in samples

| Sample | Treatment | Yield loss (%) | Cause of yield loss |
|---|---|---|---|
| SW1 | Endo | 2 | Solubilisation of cellulose |
| SW2 | Endo+xyl+man | 3 | Solubilisation of cellulose and hemicelluloses |
| SW3 | Acid | 1 | Solubilisation of hemicellulose and cellulose |
| SW4 | Acid | 0,4 | Solubilisation of hemicellulose and cellulose |
| SW5 | Endo+CCE | 4 | Solubilisation of cellulose and hemicelluloses (especially xylan) |
| HW1 | Endo | 1,4 | Solubilisation of cellulose |
| HW2 | Endo+xyl | 7,9 | Solubilisation of cellulose and xylan |
| HW3 | Endo+CCE | 16,2 | Solubilisation of cellulose and hemicelluloses (especially xylan) |
| HW4 | Steam explosion | 8,2 | Solubilization ofcellulose and xylan |

In addition to differences in pre-treatments itself, origin of pulp has also effect on yield loss with different treatments. Hardwood species such as *Eucalyptus Globulus* contain higher amounts of xylan than softwood species, which explains higher yield losses with treatments targeting xylan. It can be also said that xylan targeting treatments such as CCE might not be the best possible choice for softwood pulps rich in glucomannan, because CCE has only minimal effect on glucomannan content of pulps.

Yield losses of pulp samples were measured with compositional analysis in case of softwood samples, but compositions of hardwood samples were approximated from amounts of dissolved sugars after pre-treatments, which were used for calculation of corresponding polymer molecules. Amounts remaining were calculated with average amounts of xylan and glucomannan content of *Eucalyptus globulus.* Results gained were

arranged from lowest to highest hemicellulose content left in Table 3 for easier comparison of samples.

Table 3: Hemicelluloses left in pulp samples

| Sample | Treatment | Xylan (%) | Glucomannan (%) | Xylan + glucomannan (%) |
|---|---|---|---|---|
| SW5 | Endo + CCE | 3,17 | 5,32 | 8,49 |
| HW3 | Endo+ CCE | 7,4 | 1,5 | 8,9 |
| SW2 | Endo + xyl + man | 6,47 | 5,73 | 12,20 |
| HW4 | Steam explosion | 11,2 | 1,5 | 12,7 |
| SW3 | Acid | 7,13 | 5,78 | 12,90 |
| SW1 | Endo | 7,22 | 5,84 | 13,06 |
| HW2 | Endo + xyl | 12,61 | 1,5 | 14,11 |
| HW1 | Endo | 17,91 | 1,5 | 19,41 |

As we can see in Table 3, the most effective method for removal of hemicelluloses was clearly CCE in both softwood and hardwood samples. When examining molecular weight distribution curves in Figure 17, it is evident that signature bump usually caused by lower molecular weight hemicelluloses is missing. When comparing samples with little more hemicelluloses left (SW2, HW4, SW3, and SW1), it can be clearly seen that pulps have different kinds of composition. For example, sample SW2 has only minimal hemicellulose bump, so it has quite uniform polydispersity. Sample HW4 has clearly more hemicelluloses, which can be attributed to quite high amounts of xylan left as can be seen in Table 3. It can also be seen that samples SW3 and SW1 have quite high amounts of hemicelluloses left, but curves are also lower than in samples with more selective treatments such as CCE. This can be explained by treatment with endoglucanase and acid, which both cause lowering of cellulose DP. As for samples HW2 and HW1, it can be seen in Table 3 that treatment with endoglucanase or endoglucanase combined with xylanase clearly isn't sufficient. Both pulp samples have very high amounts of xylan left. It can be seen that combining xylanase with endoglucanase produces clear improvement to pulp hemicellulose content, but xylanase itself seems to be insufficient treatment for pulp sample high in xylan, such as one originating from *Eucalyptus*

*globulus.* The difference caused by xylanase can be seen in Figure 17, where there can be clearly seen a drop in middle weight fraction.

Table 4: Solubilities of samples

| Sample | Treatment | Average score | n |
|---|---|---|---|
| SW2 | Endo+xyl | 3 | 2 |
| SW4 | Acid | 3 | 2 |
| HW3 | Endo+CCE | 3 | 2 |
| HW4 | Steam explosion | 3 | 2 |
| SW1 | Endo | 2,75 | 4 |
| HW1 | Endo | 2,66 | 6 |
| HW2 | Endo+xyl | 2,66 | 3 |
| SW5 | Endo+CCE | 2,33 | 3 |
| SW3 | Acid | 2 | 1 |
| Softwood | | 2,66 | 12 |
| Hardwood | | 2,77 | 13 |

With this information and information about high amounts of hemicelluloses causing problems in processability and mechanical properties of regenerated fibres, it can be hypothesized that spinnability and physical properties of fibres may have some correlation to hemicellulose compositions presented in Table 3.

There has been some evidence about increasing hornification after removal of hemicelluloses and drying of pulp (Oksanen et al., 1997). In addition, it is known that CCE causes lattice transformation of cellulose crystalline structure, causing loss of reactivity and increased hornification (Arnoul-Jarriault et al., 2015). This was examined with dissolution trials after water activation of pulp samples, but there was hardly any correlation between pre-treatment and state of hornification. Every pulp sample had sufficient solubility after water activation, which was estimated in Table 4 above. As it can be seen, solubility of samples didn't have any correlation with method of pre-treatment.

The most important thing about solubilization of water activated pulp samples was the fact, that pulp samples were dissolved in DMC of 50wt%. It was known that ionic liquid would not be very compatible with excess water, so successful dissolution in pulp containing half of its mass in water was positive surprise. Because every successfully dissolved sample had DMC of 50wt%, this is not mere coincidence. It is known that water decreases the solubility of cellulose into ionic liquid through competitive hydrogen

bonding of water molecules (Zhu et al., 2006). This phenomenon is evident, because it's the basis of this same study, in which water bath is used for regeneration of cellulose.

One goal of this study is to examine how samples with different pre-treatments and different hemicellulose composition behave in spinning process, and how they affect mechanical properties of fibres produced. There has been studies about how ionic liquids can dissolve hemicelluloces such as xylan (Froschauer et al., 2013), and hemicelluloses have also been observed to cause reduction in physical properties of regenerated fibres such as Lyocell (X. Jiang et al., 2020). In following chapters, spinnability of pulp samples and mechanical properties of produced fibres will be studied, hopefully giving some insight into choosing best pre-treatment method for future studies.

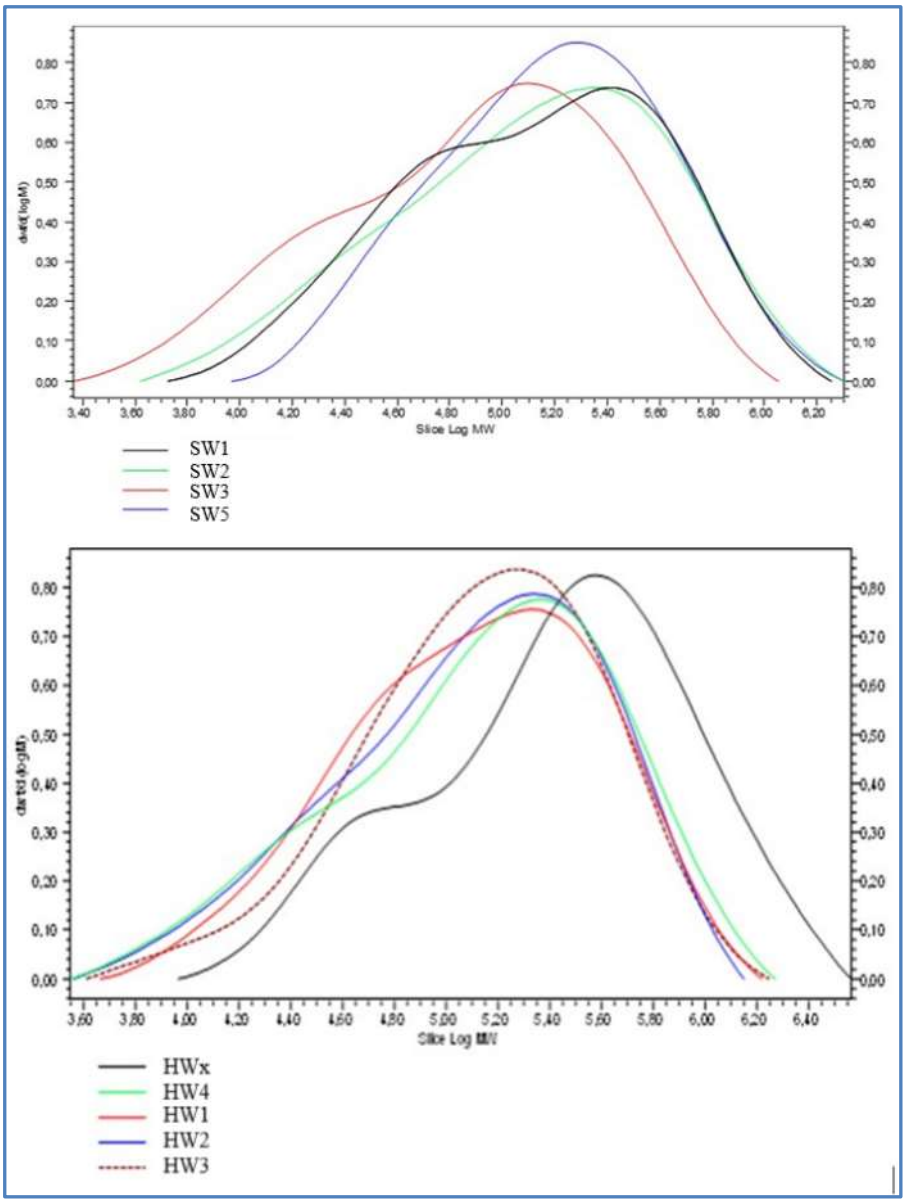


Figure 17: Molecular weight distributions of samples

## 4.2 Effect of water activation on solubility of pulp samples

The pre-treatments of the HW-and SW-pulps were necessary to adjust the molecular weight of kraft pulps to suitable level for dissolution trials. Additionally, the pre-treatments influenced the amount of hemicellulose left on pulps, and on the inner structure of pulp fibres (Spönla, 2020). As consequence, pre-treatments made the pulps more susceptible for hornification during drying, which was necessary for preservation of pulp samples between trials. In addition, water acts as coagulant in fibre spinning process utilizing ionic liquids (Michud, 2016), which are very sensitive to presence of water like explained before, which was additional reason for drying of pulp samples. Because is plenty of evidence about removal of hemicelluloses and pre-treatments such as CCE causing hornification of pulp samples (Arnoul-Jarriault et al., 2015), hornification of samples was expected in some extent. This assumption was correct, for all the pulp samples had subpar solubility at the beginning of trials. For this reason, several methods for water activation of pulp samples were studied, which will be explained in this chapter.

It has been shown that hornification decreases reactivity, water retention values, and tensile strengths of different pulps (Oksanen et al., 1997). This is the case especially when considering pulps treated for reduction of hemicelluloses such as xylan and glucomannan, with drying of pulp afterwards (Oksanen et al., 1997). The mechanism behind hornification is believed to be the collapsing of pore-structure and formation of interfibrillar linkages between hydroxyl groups of cellulose molecules, and cross linking of fibres (Fernandes Diniz et al., 2004; Letková et al., 2011). This causes irrecoverable loss of pore volume (Kekäläinen et al., 2014), but some of the swelling characteristics can still be recovered (Kekäläinen et al., 2014). It has been shown that drying intensity (temperature, time) have direct effect on extent of hornification (Letková et al., 2011). It has also been observed that hemicellulose content of pulp influenced the degree of hornification, making pulp with lower amounts of hemicelluloses more susceptible to hornification after drying (Oksanen et al., 1997).

First trials with mixing of dried pulp samples into ionic liquid at room temperature resulted in poor formation of a mixture, producing hard clumps with poor solubility. Comparison of pulp samples mixed into ionic liquid can be seen in Figure 18A, where effectivity of water activation can be clearly seen in homogeneity of suspension.

It turned out that milling of the dry pre-treated HW-and SW-pulps did not produce fine powder from the pre-treated kraft pulps like with dissolving pulp, so another approach was needed to enable their dissolution in ionic liquid. It was known that hornification can be reversed in some extent (Oksanen et al., 1997), so the first step in proper testing regime was finding the best way for water activation of pulp samples. Five different protocols for water activation of pulp sample HW1 were tried. The success of water activation methods were tested with solubilization trials, where 10wt% solutions were made from each water activated sample.

Figure 18: Comparison of suspensions before and after water activation

Solubility of sample HW1A seemed to be insufficient, resulting in visible clumps after initial mixing. After heat treatment, sample still had incompletely dissolved parts, which was confirmed with examination by optical microscope. Because solubility was clearly quite poor, method A was deemed unacceptable. From results obtained from this method, it can be deduced that DMC of 20wt% is insufficient for proper water activation of pulp sample.

In contrast to sample HW1A, solubility of sample HW1B seemed excellent. Sample had seemingly no undissolved parts after solubilization, which was confirmed with inspection by optical microscope. Because water activation with a very low consistency was a great

success, the method was chosen for further refinement in experimentation. Spinning of sample was tried, but viscosity of 10w% solution was too high for mechanical pump and 50ml plastic syringe.

To study if the pulp consistency in water activation could be increased, HW1-pulp was mixed with water in kneader. However, addition of water to adjust pulp consistency to 50% was not enough and more water was added so that pulp consistency was 20%. After mixing the sample, HWC1, was stored in fridge before further trials. Two approaches were tried to HWC1. With knowledge obtained from previous water activation experiments, activation in very small consistency was selected for sample HW1C1. Drying of sample HW1C on a petri dish (sample code HW1C2) was selected as second method for to study whether kneading of pulp helped in reversing hornification.

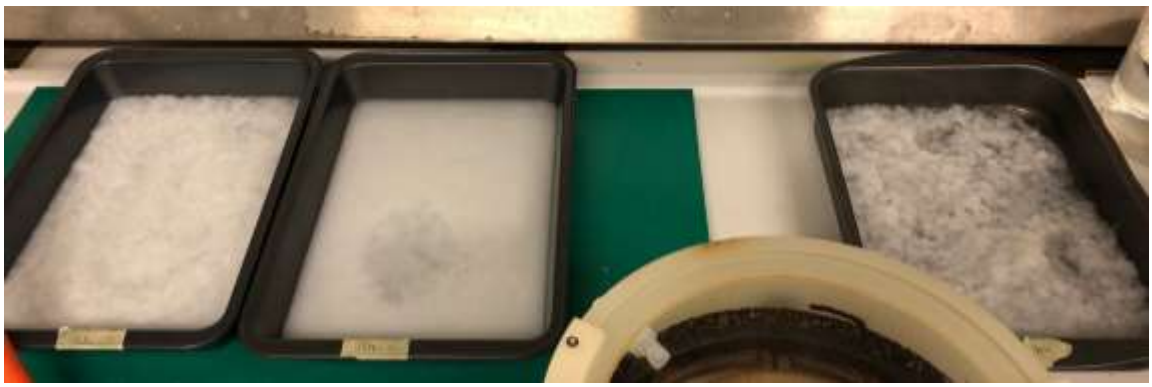

Figure 19: Different pulp samples in water activation

Mixing of the sample HW1C1 into ionic liquid was very successful, and very homogenous solution was produced. After heat treatment, dissolution of sample was deemed excellent. Solubility of sample was investigated with optical microscope, which showed only small undissolved particles.

Dissolution of sample HW1C2 was very poor after initial mixing, and heat treatment didn't improve solubility very much. The poor dissolution of sample HW1C2 was confirmed with inspection by optical microscope, which showed lots of undissolved fibres.

From these experiments, it was concluded that following water activations would be done with combination of methods B and C: Samples of DMC 20% would be mixed in kneader for 10 minutes, in overhead mixer for another 10 minutes with large amount of water and

left to swell in fridge for minimum of 24 hours. After this, pulp slurry would be dried in draft cabinet as shown in Figure 19, until minimum DMC of 50% would be reached. Finally, pulp sheet is ripped into a decanter glass, moisture content of pulp fine adjusted, and sample placed into fridge for stabilization of moisture content.

From these trials, it can be deduced that selected method for water activation has huge impact on reversing effects of hornification. Previously hornification was thought to be permanent loss of pulp characteristics such as water retention value, reactiveness, loss of strength properties, and stiffening of fibres (Oksanen et al., 1997; Jayne, 1944 as cited in Fernandes Diniz et al., 2004). Nowadays also other methods than water activation have been reported for restoring these properties to dried pulp, including beating (Kitayama et al., 1983 as cited in Fernandes Diniz et al., 2004), with addition of sucrose or glycerol (Higgins and Mckenzie, 1963 as cited in Fernandes Diniz et al., 2004), by cooking pulp in alkali (Weise et al., 1998 as cited in Fernandes Diniz et al., 2004), or steam treating of pulp (Fernandes Diniz et al., 2004).

## 4.3 Spinnability of samples with different pre-treatments

Samples with different concentrations, solubilities, durations of heat treatments, and their spinnabilities are summarized in Table 7.

Table 5: Hemicellulose compositions of pulp samples

| Sample | Treatment | Xylan (%) | Glucomannan (%) | Xylan + glucomannan (%) |
|---|---|---|---|---|
| HW1 | Endo | 17,91 | 1,5 | 19,41 |
| HW2 | Endo + xyl | 12,61 | 1,5 | 14,11 |
| SW1 | Endo | 7,22 | 5,84 | 13,06 |
| SW3 | Acid | 7,13 | 5,78 | 12,90 |
| HW4 | Steam explosion | 11,2 | 1,5 | 12,7 |
| SW2 | Endo + xyl + man | 6,47 | 5,73 | 12,20 |
| HW3 | Endo+ CCE | 7,4 | 1,5 | 8,9 |
| SW5 | Endo + CCE | 3,17 | 5,32 | 8,49 |

As it can be seen, it is quite clear that viscosity of both 10 wt% and 8 wt% solutions were too high for successful spinning of fibres, resulting in either serious struggling of mechanical pump, or “noodle” like, very weak fibres which broke down before winding up from the spin bath, which can be seen in Figure 20. Only when solutions were diluted into cellulose concentration of 5 wt%, viscosities of dopes were low enough to allow

successful extrusion through nozzle, and high enough to coagulate into sufficiently strong fibres. Interestingly, dopes which were dissolved in two steps from 8 wt% to 5 wt% had better spinnability than dopes which were dissolved into 5 wt% at once.

When examining spinnability of dopes, two main factors are usually considered: Draw ratio of samples, and uninterrupted running time of spinning. Because dope sizes were quite small and system was prone to failures such as fibres spinning out of godet, uninterrupted running time of spinning system was difficult to measure. Draw ratios were also very difficult to determine because of struggling of the pump, which produced lower output than selected speed on the display of the pump. However, spinnability of samples can be compared through the take-up velocity of godet.

Table 6: Mechanical properties of fibres

| Sample | SW1 | SW2 | SW3 | SW4 | SW5 | HW1 | HW2 | HW3 | HW4 | Viscose | Lyocell |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Viscosity (ml/g) | 450 | 430 | 440 | 540 | 450 | 430 | 430 | 460 | 450 | NA | NA |
| Mw (kDa) | 250,53 | 241,8 | 148,65 | 293,32 | 265,1 | 224,7 | 224,5 | 225 | 233 | NA | NA |
| Take-up velocity max (m/s) | 0,32 | NA | 0,36 | NA | 0,32 | 0,19 | NA | 0,06 | 0,06 | NA | NA |
| Elongation avg (%) | 13,08 | NA | 11,74 | NA | 21,72 | 4,76 | NA | 12,5 | 11,5 | 18,99 | 8,7 |
| Maximum force (cN) | 28,80 | NA | 23,67 | NA | 22,43 | 6,15 | NA | 15,3 | 15,4 | 3,44 | 4,51 |
| Tenacity (cN/dtex) | 0,47 | NA | 1,06 | NA | 1,07 | 0,75 | NA | 1,08 | 0,71 | 2,67 | 3,27 |
| Initial modulus (cN/dtex) | 27,05 | NA | 37,91 | NA | 26,56 | 32,62 | NA | 41,7 | 24,1 | 60,61 | 55,87 |
| Linear density (dtex) | 76,19 | NA | 22,45 | NA | 21,28 | 8,46 | NA | 14,2 | 22 | 1,29 | 1,38 |

While samples originating from softwood had generally better spinnabilities, softwood sample treated with endoglucanase and xylanase behaved worse than its hardwood counterpart. When comparing the spinnability of hardwood and softwood samples, softwood samples had generally better spinnabilities compared to hardwood samples. When examining intrinsic viscosities and average molecular weights of endoglucanase treated samples SW1 and HW1, it can be seen that both are higher in SW1. When examining maximum take-up velocities in these two samples, it can be seen that softwood sample has a little bit better spinnability, but the difference isn't as drastic as with other hardwood samples when being compared to their softwood counterparts. When examining hemicellulose contents of these samples in Table 5, it can be seen that sample HW1 contains significantly more total hemicelluloses, with way over twice the amount of xylan compared to SW1. When examining the MWD -curves in Figure 17, there doesn't seem to be significant differences in fractions, when differences in hemicellulose content are known. In this case, higher intrinsic viscosity and average molecular weight might be one of the reasons behind better spinnability.

However, hardwood sample treated with endoglucanase and xylanase (HW2) had better spinnability compared to similarly treated softwood sample (SW2). In this case, softwood sample SW2 had still higher intrinsic viscosity and average molecular weight compared to hardwood HW2, the spinnability of softwood sample was worse.

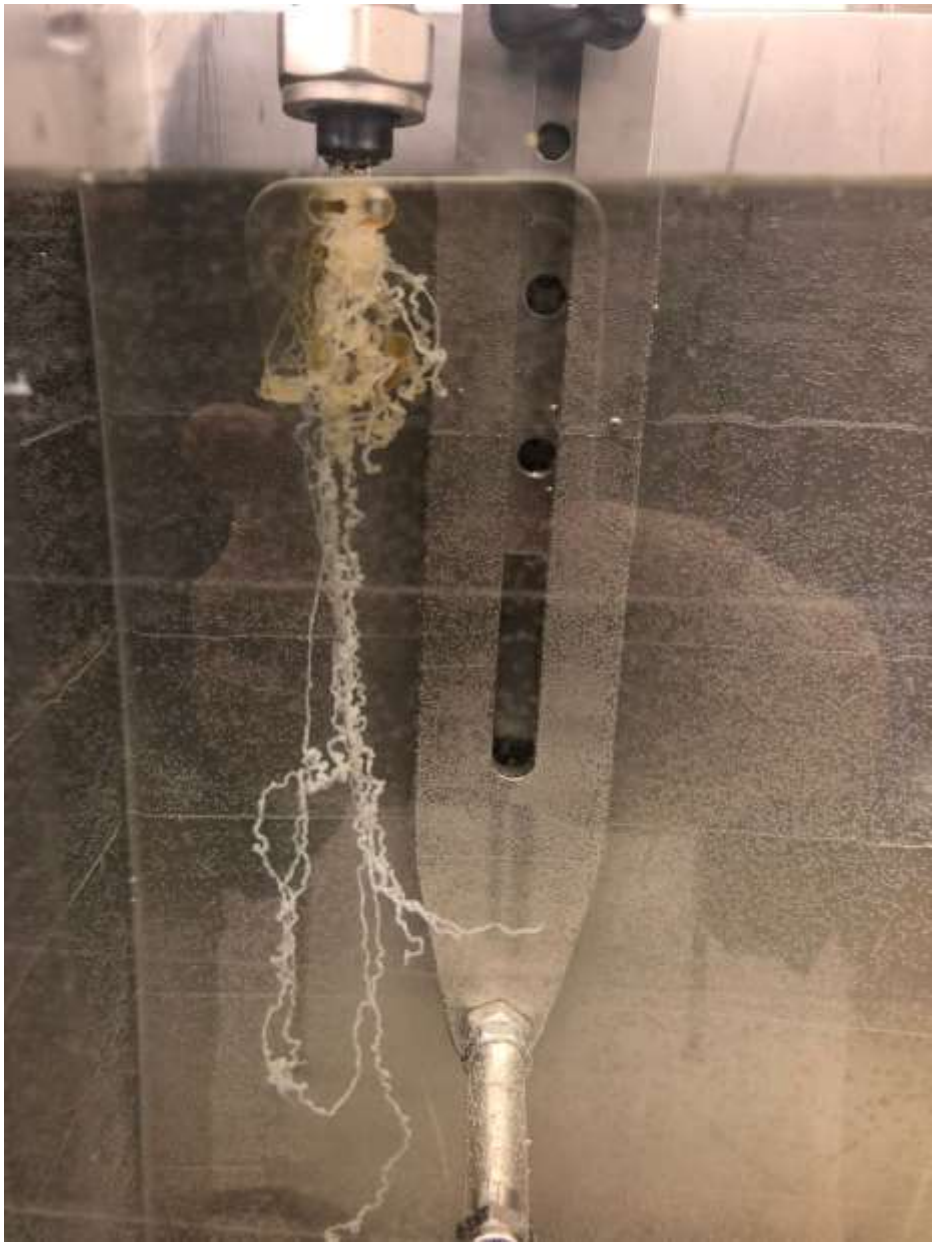

Figure 20: Failed spinning attempt

When examining molecular weight distribution charts in Figure 17 and hemicellulose composition of samples in Table 5, it can be seen that sample SW2 has less hemicellulose in general, but also less xylan than in its hardwood counterpart. Molecular weight distribution charts of both of these samples are seemingly similar, but sample HW2 has clearly higher high-molecular weight fraction. Neither of these samples were good enough to produce proper fibres though. If none of the samples treated only enzymatically

were spinnable, it could be deduced that treatment with enzymes is insufficient to produce spinnable fibres. This isn't the case though, because samples treated with only endoglucanase behaved way better than samples treated with additional hemicellulases. Sample HW1 has the highest content of total hemicelluloses and xylan from all the samples, so in theory, it should behave worse in trials than samples SW2 and HW2. From these samples, sample HW2 has almost twice the xylan content of SW2, even though total hemicellulose content between these two samples is similar. Between samples treated only enzymatically, there doesn't seem to be any correlation between spinnability and hemicellulose content of pulp samples.

Table 7: Concentrations and spinnabilities of pulp samples

| | Sample | Water activation | Solubility | Time (h) | Viscosity | Spinnability | Notes |
|---|---|---|---|---|---|---|---|
| SW | SW1 (Endoglucanase) 10% | No | Bad | 3 | High | No | |
| | SW1 (Endoglucanase) 10% | No | Bad | 1 | High | No | |
| | SW1 (Endoglucanase) 10% | Yes | Good | 26 | High | No | |
| | SW1 (Endoglucanase) 10% | Yes | Good | 98 | High | No | |
| | SW1 (Endoglucanase) 5% | Yes | Good | 52 | High | No | |
| | SW1 (Endoglucanase) 5% | Yes | Medium | 24 | Medium | Yes | Two-step dissolution |
| | SW2 (Endoglucanase + xylanase) 10% | No | Bad | 3 | High | No | |
| | SW2 (Endoglucanase + xylanase) 10% | Yes | Good | 100 | High | No | |
| | SW2 (Endoglucanase + xylanase) 5% | Yes | Good | 50 | High | No | |
| | SW3 (H2SO4) 10% | No | Bad | 1 | High | No | |
| | SW3 (H2SO4) 5% | Yes | Medium | 50 | High | Yes | Two-step dissolution |
| | SW4 (H2SO4 with different MWD) 10% | Yes | Good | 101 | High | No | |
| | SW4 (H2SO4 with different MWD) 5% | Yes | Good | 125 | High | No | |
| | SW5 (Endoglucanase + CCE) 10% | No | Bad | 1 | High | No | |
| | SW5 (Endoglucanase + CCE) 10% | Yes | Good | 48 | High | No | |
| | SW5 (Endoglucanase + CCE) 10% | Yes | Bad | 50 | High | No | Dissolution in higher DMC |
| | SW5 (Endoglucanase + CCE) 5% | Yes | Good | 24 | Medium | Yes | One-step dissolution |
| HW | HW1 (Endoglucanase) 10% | No | Bad | 1 | High | No | |
| | HW1 (Endoglucanase) 10% | Yes | Good | 2 | High | No | |
| | HW1 (Endoglucanase) 10% | Yes | Good | 24 | High | No | |
| | HW1 (Endoglucanase) 10% | Yes | Good | 24 | High | No | |
| | HW1 (Endoglucanase) 8% | Yes | Medium | 49 | High | No | |
| | HW1 (Endoglucanase) 5% | Yes | Good | 48 | High | No | |
| | HW1 (Endoglucanase) 5% | Yes | Medium | 48 | Medium | Yes | Two-step dissolution |
| | HW2 (Endoglucanase + xylanase) 8% | Yes | Medium | 48 | High | No | |
| | HW2 (Endoglucanase + xylanase) 5% | Yes | Good | 96 | Low | No | Diluted from 8% sample |
| | HW2 (Endoglucanase + xylanase) 5% | Yes | Good | 48 | High | No | |
| | HW3 (Endoglucanase + CCE) 8% | Yes | Good | 24 | High | No | |
| | HW3 (Endoglucanase + CCE) 5% | Yes | Good | 49 | Medium | Yes | Diluted from 8% sample |
| | HW4 (Steam explosion) 8% | Yes | Good | 24 | High | No | |
| | HW4 (Steam explosion) 5% | Yes | Good | 49 | Medium | Yes | Diluted from 8% sample |
| REF | REF1 (Dissolving pulp) 10% | No | Good | 1 | High | No | |
| | REF1 (Dissolving pulp) 10% | No | Good | 24 | High | No | |
| | REF1 (Dissolving pulp) 8% | No | Good | 49 | High | No | Diluted from 10% sample |
| | REF1 (Dissolving pulp) 5% | No | Good | 73 | High | No | Diluted from 8% sample |

Next pair of samples, acid treated softwood sample (SW3) and hardwood sample treated with steam explosion (HW4) seem to have quite similar MWD -curves, even though hardwood sample seems to be little richer in high molecular weight fractions. This is understandable, because acid treatment isn't very selective towards hemicellulose, and causes also depolymerization of cellulose, which usually has the highest degree of

polymerization in lignocellulosic biomass. Both samples have similar percentage of total hemicelluloses, but sample treated with steam explosion has higher amounts of xylan left. In contrast, softwood pulps naturally have higher amounts of glucomannan, including acid treated softwood sample SW3. As we can see in Table 6, spinnability of acid treated softwood sample was significantly higher, achieving six times higher maximum take-up velocity. In this case, sample with higher xylan content produced inferior spinnability.

Lastly, samples with absolute lowest amounts of hemicelluloses (especially xylan) left are the ones treated with CCE and endoglucanase: Softwood sample SW5, and hardwood sample HW3. Once again, even though total hemicellulose content in these samples is similar, hardwood sample contains more xylan whereas softwood sample has more glucomannan. Both samples produced spinnable fibres, but as with other hardwood samples, spinnability was nowhere near as good as with softwood sample. Once again, MWD -curves of both samples were very narrow, and almost identical, though all the hardwood fractions were little lighter than ones in softwood sample. Even though these samples had similar MWD -curves, softwood sample SW5 had noticeably higher Mw than hardwood sample HW3. In this case, differences in spinnability could be explained by differences in hemicellulose composition, or in Mw of samples.

As we can see in Table 6, all hardwood samples had lower take-up velocities than softwood samples. Basically this means that every hardwood fibre broke at low rotating speed of the godet, whereas softwood samples such as acid treated SW3 had good spinnability.

In many cases, it does seem that samples higher in xylan perform worse in spinning experiments. However, even though samples HW3 and HW4 had low amounts of xylan, their spinning was difficult. One possible reason for poor spinnability might be the naturally shorter fibre length and degree of polymerization of cellulose molecules originating from hardwood. That might not be the case though, because molecular weight distribution curves of softwood and hardwood samples don’t have that many differences in their high molecular weight fraction. Acid treated softwood sample SW3 with best spinnability had the highest fraction of shorter polymer chains of all the samples, but also the lowest amount of long polymer chains. From this observation, it could be deduced that best spinnability is caused by overall low, but steady molecular weight distribution. This either isn’t the case though, because molecular weight distribution of sample SW5

had high contrast to curve of SW3: Whereas SW3 had quite low and steady distribution, sample SW5 had high fraction of molecules of high molecular weight, but very low amounts of smaller molecules. One other possible reason for poor spinnability could be human error in spinning, because spinning equipment relied heavily on handiwork, and methods became more refined as time went. This couldn't explain why every single hardwood sample behaved worse in spinning trials though, so the reason must be in compositional differences between hardwood- and softwood samples.

## 4.4 Mechanical testing

Results of mechanical testing are collected in Table 6, along with results from commercial viscose rayon for reference. As expected from spinnability of samples, softwood samples also exhibit generally better mechanical properties. Maximum force required to break fibres from sample SW1 was almost twice as high as with strongest fibre made from hardwood samples, HW4. This isn't even proper comparison though, because strength properties should be compared between samples with similar pre-treatments. When comparing endoglucanase treated softwood sample SW1 to hardwood sample HW1 with similar pre-treatment, it can be seen that maximum force required to break sample HW1 is almost five times lower than its softwood counterpart. Similar results can be observed with elongation, which is about three times higher in softwood sample SW1. Values for maximum strength and elongation don't tell the whole truth though: Sample HW1 exhibits higher initial modulus and tenacity compared to sample SW1. Because tenacity is defined by dividing breaking load with linear density of sample, it is better variable for comparison between different fibres. Difference between linear densities of fibres spun from samples SW1 and HW1 are also quite drastic: Linear density of sample SW1 is almost ten times higher than with sample HW1. Because linear density is defined by mass of fibre per length, it doesn't specify whether fibre has high density, or thickness. In case of samples SW1 and HW1, it can be definitely seen from Figures 21A and 21B that sample SW1 has way higher cross-sectional area compared to HW1. This difference in thickness could be attributed to lower draw ratio, but difference between take-up velocities suggests that sample SW1 should have had higher draw ratio and should thus have more stretched out appearance.

Samples SW5 and HW3 were both pre-treated with endoglucanase and CCE, and both had similar amounts of total hemicelluloses as seen in Table 5, but sample HW3 had

naturally higher amounts of xylan, whereas sample SW5 had more glucomannan. As with previous pair of samples, take-up velocity of hardwood sample was over five times lower than with softwood sample SW5. Elongation of softwood sample SW5 was almost twice as high than with hardwood sample HW3. Compared to previous pair of samples though, this pair had quite similar mechanical properties: Maximum force required for breakage of fibre was only about ¼ higher with softwood sample SW5 as was the linear density of softwood sample SW5, resulting in almost identical tenacities of fibres. This is surprising, because poor spinnability of sample HW3 was expected to result in fibres with insufficient strength properties. Even though elongation of sample HW3 was worse than with sample SW5, it was close to every other fibre sample in this study. Sample HW3 also exhibits highest initial modulus of all the fibres in this study, which makes it one of the most promising samples being studied.

Last pair of samples left have a little bit worse comparability than previous sample, originating from different kinds of pre-treatments: Sample SW3 was treated with dilute acid hydrolysis which also affects DP of cellulose, whereas sample HW4 was treated with quite gentle method of steam explosion, which mainly affects xylan content of pulp sample. Even though these samples had seemingly different pre-treatments, their amounts of total hemicelluloses are quite close to each other as can be seen in Table 5. Once again, hardwood sample HW4 has higher amount of xylan left, whereas softwood sample has more glucomannan. Once again take-up velocity for hardwood sample was six times lower than with softwood sample. For these samples, values for elongation and linear density were similar, but tenacity and initial modulus were vastly superior with softwood sample. The reason for these differences might not be in the hemicellulose composition of samples, but in average Mw: This acid treated sample had way lower average molecular weight than any other sample, as seen in Table 1. This might have caused lower viscosity of the dope, which could have caused pump to struggle less than with other samples, thus producing fibres with more uniform structure.

When compared to results from commercial viscose fibre, all of these properties were inferior. It must be remembered though, that manufacturing process for viscose rayon was invented over a hundred years ago and has thus been refined much further than this process. When comparing fibres, it would be better to choose processes as similar as possible. For that reason, fibres from this study will also be compared to Lyocell fibres.

Properties for Lyocell were obtained from study made by (Ramamoorthy et al., 2015), and are collected in Table 6.

As can be seen in Table 6, Lyocell fibres exhibit lower values for elongation compared to any other fibres in this study, or viscose rayon. Tenacity of Lyocell fibres is vastly superior to any of the samples in this study and is noticeably higher than with viscose. Initial modulus is a little bit lower than with viscose, but once again, significantly higher compared to samples in this study. Superior physical properties of Lyocell fibres can be explained by higher orientation and crystallinity compared to viscose. This increased orientation and crystallinity are a result of air gap in Lyocell process, which viscose process lacks (S. Zhang et al., 2018). In theory, air gap in this study should also cause improved physical properties to fibres compared to viscose process, but as said before, this process is still in development, and in many cases successful drawing of fibres relies heavily on dexterity of process operator.

From fibres studied, acid treated sample SW3, endoglucanase and CCE treated sample SW5, and hardwood sample HW3 treated with endoglucanase and CCE exhibited the best mechanical properties. All of these had similar values for elongation, tenacity, and initial modulus. Otherwise, these samples don't seem to have too many similarities other than amount of total hemicelluloses with samples treated with CCE and endoglucanase. Even with those samples, hemicellulose composition differs in amounts of xylan and glucomannan. One possible reason for successful production of fibres from these samples might be the viscosity of the dope: In case of samples HW3 and SW5, low amounts of hemicellulose might have caused decrease in viscosity. Acid treated sample SW3 had higher amounts of hemicelluloses, but decreased Dp of cellulose might have compensated this increased viscosity caused by hemicelluloses. Other possible reason for differences in properties of fibres might be errors in operation: Because operation relied heavily on handiwork of operator, human error is possible.

## 4.5 Microscope examination

Examinations with optical microscope were conducted to ensure proper dissolution of pulp fibres, and for closer examination of produced regenerated fibres. Solutions were inspected with both 4x and 10x magnifications, whereas inspection of spun fibres was conducted also with 25x magnification for closer inspection of fibre structure.

### **4.5.1** Examination of dopes

In Figure 21A, we can see undissolved cellulose particles from dry pulp sample SW1 after dissolution. Because every dry pulp sample had similar behavior, hornification of pulp fibres during drying of samples was suspected. For this reason, water activation of dried pulp samples was studied for reversal of hornification to some extent, which was found to improve solubility drastically (see chapter 4.2). As we can see in Table 7, solubility of every sample became good enough for spinning trials (even though spinning of every sample wasn't successful). The difference in solubility of dopes prepared from pulp sample SW1 with and without water activation can be seen in Figures 21A and 21B. It can be clearly seen that there are huge amounts of undissolved particles before water activation in Figure 21A, which are almost completely absent in water activated sample in Figure 20B. Similar behavior was observed with every other pulp sample, which gave enough reason to conduct trials for water activation.

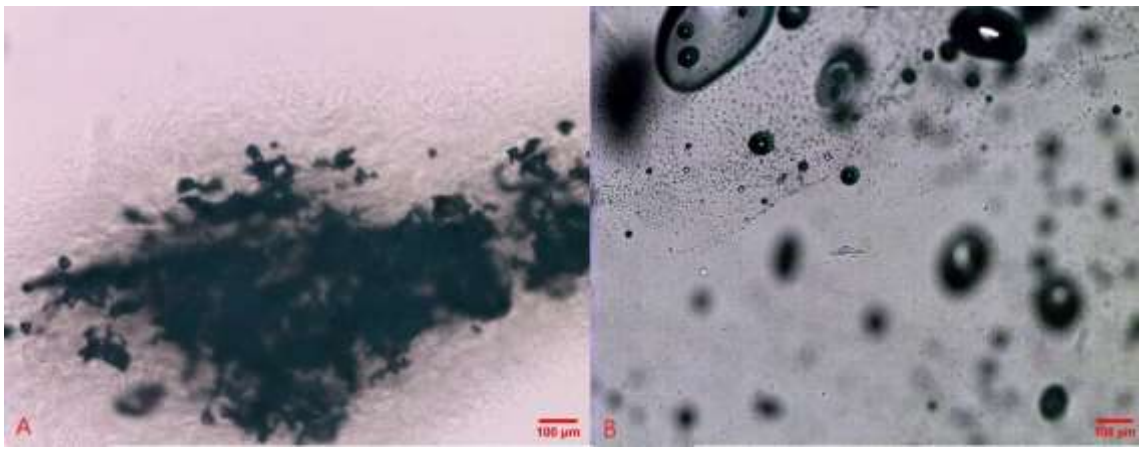


Figure 21: Sample SW1 before (A) and after (B) water activation (10x)

### **4.5.2** Examination of regenerated fibre samples

As with solution samples, finished fibres were also studied with microscope to find out if dopes made from different pulp samples produced noticeable structural differences in fibres. Unfortunately, because volumes of spinnable dopes were low, take-up velocities in spinning had to be adjusted in quite short time. Because of this, dimensions of every fibre sample had significant variation, so the thickness of fibres in microscope images alone isn't very reliable way of determining the quality of spun fibres. However, images could be utilized by analyzing surface structure, and uniformity of dimensions.

When comparing regenerated fibres from endoglucanase treated pulps SW1 and HW1 in Figures 22A and 22B, we can see clear differences in thickness of fibres, earlier. Additionally, the fibres have different surface structure, the visible cracking in these fibres differ from each other. In softwood sample SW1 which had significantly higher spinnability than its hardwood counterpart HW1, cracks seem to be distributed more evenly. Because better spinnability resulted in more even cracking of fibre surface, it was suggested that formation of the cracks might have happened because of uneven speed of extrusion, which was especially noticeable when viscosity of dope was too high. Same problems in extrusion speed seemed to be a reason for large variations in fibre diameter. Like extrusion speed, take-up velocity can also cause differences in surface morphology. In this case, softwood samples could be generally spun with high take-up velocities, whereas hardwood samples were hardly spinnable even with lowest possible velocity. Other possible reason might be delays in spinning caused by broken fibres or other problems in runnability of process, which might allow some parts of the spun fibre higher amounts of time to swell in coagulation bath.

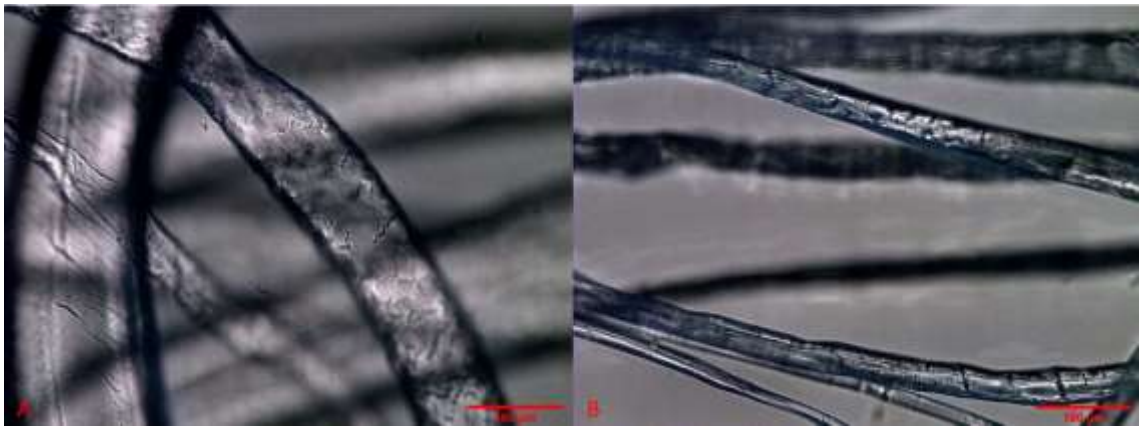

Figure 22: Fibres from sample SW1 (A) and HW1 (B) (25x)

The microscope images from regenerated fibres from endoglucanase- and cold caustic extraction treated pulp samples SW5 and HW3 can be seen in Figures 23A and 23B, respectively. When examining the fibres, sample SW5 lacks any major surface irregularities, unlike sample HW3, which has same kind of grooves like the previous hardwood sample HW1 in Figure 22B. Smooth morphology of sample SW5 could be attributed to excellent drawability of the sample, which supports the hypothesis about

cause of the irregular morphology of fibres explained before.

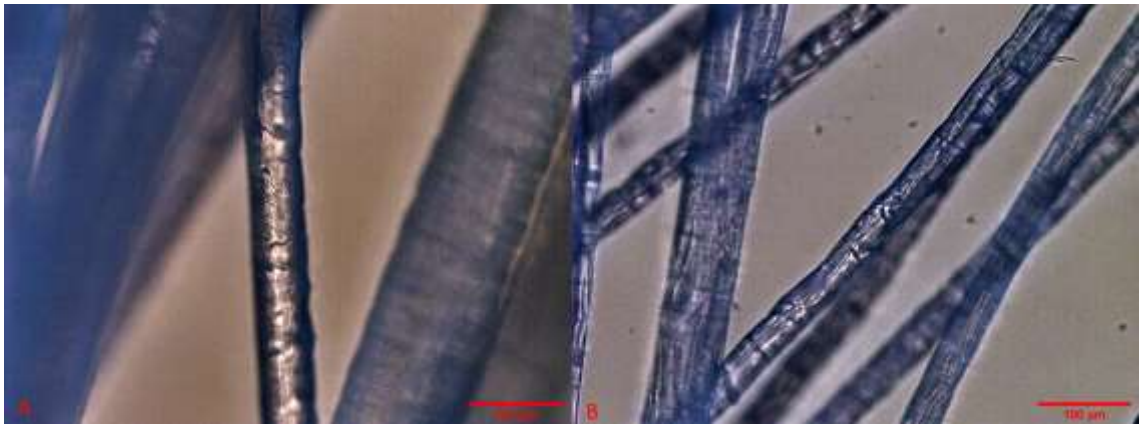

Figure 23: Fibres made from pulp SW5 (A) and HW3 (B) (25x)

The most interesting contrast in regenerated fibres can be found between fibres spun from acid treated pulp sample SW3 (Figure 24A), and fibres spun from steam exploded pulp sample HW4 (Figure 24B). As can be seen in Figure 24A, fibres drawn from dope SW3 exhibit very bumpy structure, whereas fibres drawn from pulp sample HW4 seem to be warped, while quite smooth.

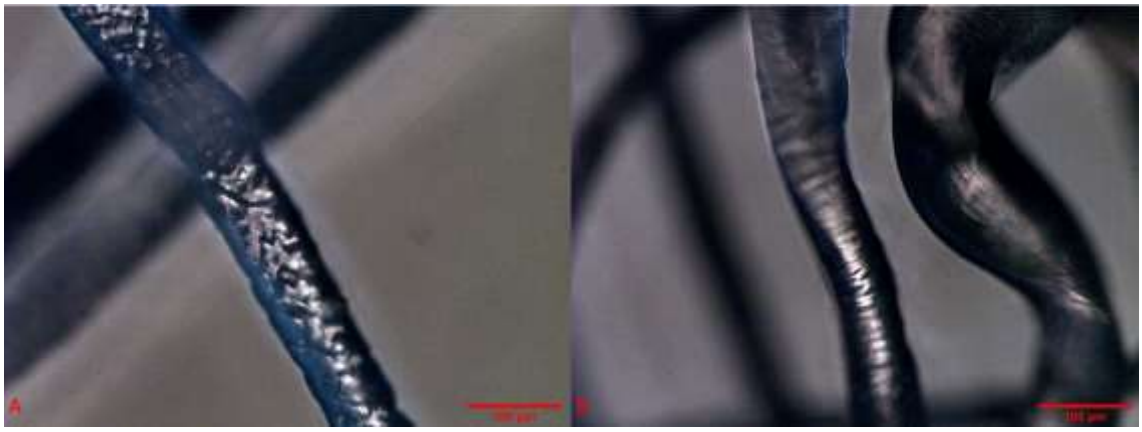

Figure 24: Fibres made from sample SW3 (A) and HW4 (B) (25x)

Even though this fibre sample has bumpy structure, the dope of SW3 had excellent spinnability, resulting in highest take-up velocity of all samples. Same kind of surface morphology have previously been reported by (Vehviläinen et al., 2015) with fibres spun into 10% sulphuric acid. In this study, formation of such surface morphology was attributed to fast coagulation and rapid diffusion of chemicals inside fibre.

Lastly, sample HW4 has quite different morphology compared to any other hardwood samples in this study. It seemed that these fibres had more swollen structure than other

fibres in this study, which indicate too low take-up velocity during spinning. Fibres seem to be quite warped though, which might be caused by too high viscosity, which causes “noodling” of fibres, which can be seen in Figure 20.

As a general observation, shape of cross-sections of almost every fibre in this study are similar to lyocell fibres in many studies (Grieve, 1996; G. Jiang et al., 2012), which is understandable because manufacturing process is also similar. Smooth surface morphology of most of the softwood samples is also similar, which can be attributed to better drawability of softwood samples compared to hardwood samples. Another possibility for different surface morphologies is the differences in hemicellulose composition of samples. There has been some evidence of hemicellulose together with lignin causing loss of orientation for cellulose molecules in man-made fibres, which might result in irregularity of surface structure of produced fibres (Ma et al., 2018)

When examining fibres deemed best in mechanical testing (SW3, SW5, and HW3) every fibre has same kind of structural similarities: Thickness of fibres are quite low compared to some weaker fibres, which might indicate better stretching during spinning, and thus better orientation of molecules. In addition, fibres have quite regular structure regarding surface and thickness, which might be caused by good spinnability of fibres. Good spinnability of fibres indicates good runnability of process, which means viscosity of dopes and composition of samples must be good.

# 5 CONCLUSIONS

The goal of this thesis was to study effects of different pre-treatments and chemical compositions on solubility of pulp samples into a novel ionic liquid, and how different pulp compositions and process parameters affect spinnability of fibres with dry-jet wet spinning technique.

Pulp samples were dried after the different pre-treatments and they were clearly hornified when received, which could be seen in poor dissolution properties of pulp samples at the beginning of this study. For this reason, different methods for water activation of pulp samples were tried. Method with mechanical kneading of pulp sample combined to swelling in large amounts of water was deemed the best method for water activation, which was confirmed in following dissolution trials, where signs of hornification became absent. It was assumed that different pre-treatments might result in different states of hornification in different pulp samples, but there was no evidence of this phenomenon: Every sample had poor solubility before water activation, but solubility became equally good afterwards.

Different pulp samples had differing amounts of total hemicelluloses, but also different hemicellulose compositions: Softwood samples contained more glucomannan, whereas hardwood samples contained more xylan. Differences in solubility could not be identified: there was no clear correlation between hemicellulose composition and solubility of pulp samples into ionic liquid. This observation was similar to results in literature, in which ionic liquids have been shown to dissolve hemicellulose as well as cellulose. It was interesting to notice that against presumptions, amount of water in pulp samples didn't adversely affect dissolution of pulp samples. It is known that ionic liquids have low tolerance for water. Because dissolved pulp samples in this study had DMC of 50wt%, there were quite large amounts of water involved.

Amount of xylan in pulp samples was assumed to adversely affect spinning of fibres, causing problems with viscosity of dope, and thus spinnability of fibres and runnability of process. There has been some evidence about hemicelluloses adversely affecting spinning processes, in case of Lyocell for example. In this case, there were some agreeable results concerning effects of xylan. From total of nine pulp samples, only six were spinnable enough to produce fibres for mechanical testing. From these samples,

three were clearly superior to other samples: Softwood and hardwood samples treated with endoglucanase and CCE, and softwood sample treated with steam explosion. Samples treated with endoglucanase and cold caustic extraction resulted in two of the less hemicellulose containing samples in this whole study. The third sample was softwood sample treated with acid hydrolysis. It had little bit higher amount of total hemicelluloses compared to other samples, but it also had significantly lower intrinsic viscosity of all samples in this study, which might have compensated the increased viscosity caused by hemicelluloses. In addition to overall low hemicellulose composition of these samples, all samples had below average amounts of xylan left. From this, it can be concluded that viscosity of the sample is one of the most important factors regarding spinnability, in which amount of xylan is responsible. It could also be observed during experimentation: cellulose concentration of the dope had to be lowered to 5wt% before samples were spinnable and even after that, samples had to be pre-heated to reduce viscosity and prevent struggling of the pump. Because pump had problems with viscosities of the solutions even in best cases, real values for draw ratios couldn't be determined. Spinnability of samples was determined by runnability of process and take-up velocity though, which made it possible to compare results.

Microscope studies confirmed the uniform structure of best three samples. This uniformity could be attributed to good spinnability, which caused uninterrupted drawing and possibly favorable orientation of cellulose molecules.

From this study, it can be concluded that dope viscosity has great effect on processability of pulp samples. Hemicellulose content of samples has direct effect on viscosity, so amount of hemicelluloses probably have negative effect on processability. Some results from this study might have been influenced by human error, but for example, results for hardwood samples were consistently worse in spinning, and mechanical testing.

The tenacity of the produced fibres was low. The reason for this might be the early stage in experimentations of this process. For further studies, the improvement of the tenacity of the fibres is important. The rheology analyses of the dopes may give further insights to the needed heating and better pre-heating methods to accurately adjust the spinning temperature. In addition, additional drying of pulp samples after the pre-treatments should be avoided to overcome the different hornification of pulps. For further studies, dopes

from never dried samples are of interest. For example, better methods for pre-heating of dopes could be tried, or MWD:s of samples could be further modified for this process.

Fibres from this study were one of the first fibres produced from hemicellulose containing kraft pulps. Even though fibres produced didn't have physical properties as good as with commercial fibres such as viscose rayon, results are promising. In the future, there might be man-made fibres with quite high amounts of hemicellulose left.

Other possible subject for future studies might be the effect of hemicelluloses to the color, tenacity, and other physical properties of produced fibre. By studying the composition of coagulating bath after processing, it might reveal how large portion of the dope actually causes the formation of fibre, and how large losses of yield this process has.

Finally, one very important aspect of this spinning process is its environmental impact. For this reason, process must have good recyclability of chemicals, which has not been studied yet. Some of the hemicelluloses of pulp might remain in coagulating bath, making recycling of ionic liquid more difficult. Carbon economy of this process has not been studied yet, which is also one possible research problem for the future.

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